Inorg. Chem. **2006**, *45*, 1560–1574

Inorganic Chemistry
Article

Synthesis and Characterization of Silver(I) Coordination Networks Bearing Flexible Thioethers: Anion versus Ligand Dominated Structures

Mohamed Osman Awaleh,[†] Antonella Badia,[†] François Brisse,*,[†] and Xian-He Bu[‡]

*Département de Chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville,
Montréal Québec, Canada H3C 3J7, and Department of Chemistry, Nankai University,
Tianjin 300071, P. R. China*

Received August 8, 2005

This report describes the synthesis and X-ray characterization of a series of $\mathbf{L}^n$AgX complexes wherein $\mathbf{L}^n$ = PhS(CH$_2$)$_n$SPh (n = 2, 4, 6, 10) and X = $CF_3SO_3^-$, CF_3COO^-, $CF_3CF_2COO^-$, $CF_3CF_2CF_2COO^-$, NO_3^-, and ClO_4^-. This study was undertaken in order to rationalize the structure of the coordination networks formed as a function of the anion coordinating strength and the ligand structure. The following complexes were examined: with $\mathbf{L}^2$, $CF_3SO_3^-$ (**1**), CF_3COO^- (**2**), ClO_4^- (**3**); $\mathbf{L}^4$, $CF_3SO_3^-$ (**4**), CF_3COO^- (**5**), $CF_3CF_2COO^-$ (**6**), $CF_3CF_2CF_2COO^-$ (**7**); $\mathbf{L}^6$, $CF_3COO^-\cdot H_2O$ (**8**), $CF_3CF_2COO^-$ (**9**), $CF_3CF_2CF_2COO^-$ (**10**); and $\mathbf{L}^{10}$, NO_3^- (**11**). The anions selected are classified in three groups of increasing coordinating strength: perchlorates, fluorosulfonates, and perfluorocarboxylates. Except in two cases, all complexes form 2D-coordination networks. The 2D-network in **1** ($\mathbf{L}^2$, $CF_3SO_3^-$) is made up of Ag(I) and $\mathbf{L}^2$, while the anion is only a terminal co-ligand that completes the trigonal coordination around Ag(I). In **4** ($\mathbf{L}^4$, $CF_3SO_3^-$), a 1D-coordination polymer, $[Ag–\mathbf{L}^4–]_\infty$, is observed where the anions are coordinated to Ag(I) in a trigonal fashion. The perfluorocarboxylates form tetrameric units in a zigzag shape, but only with the $\mathbf{L}^4$ ligand. In these (**6** and **7**), the silver–silver distances are very short, especially those of the central bond, indicating the presence of weak Ag–Ag interactions. Dimers, with short silver–silver distances, are observed with ligands $\mathbf{L}^2$ and $\mathbf{L}^6$ and perfluorocarboxylates. In **8** ($\mathbf{L}^6$, $CF_3COO^-\cdot H_2O$), a 3D channel-like structure is built through water molecules that connect adjacent layers. An unusual stoichiometry is noted in **3** ($\mathbf{L}^2$, ClO_4^-, acetone); Ag:L is 4:2.5. In **11** ($\mathbf{L}^{10}$ and NO_3^-), the nitrate acts as a bidentate ligand and an $[Ag–NO_3–]_\infty$ chain is formed. Adjacent chains are linked by the $\mathbf{L}^{10}$ ligands into a 2D-coordination network.

Introduction

The self-assembly of metal−organic coordination polymers is attracting great attention because of their potential as functional materials.[1] The properties of materials composed of coordination networks depend on their network topology. Thus, it is pertinent to understand and control the subtle factors that influence the formation of the supramolecular networks. However, in metal−organic crystal engineering, predicting the coordination polymer topology when flexible ligands are used is more difficult due to the numerous factors affecting the formation of the supramolecular framework. For a given metal and a specific set of ligands, these factors include the recrystallization solvent used,[2] the nature of the counteranions,[3] and the metal-to-ligand ratio.[4] On the other hand, the anion coordination chemistry is a promising area because of its application in anion template assembly, ion-pair recognition, and the role of anions in supramolecular chemistry.[5,6] Besides their size and geometry, the coordinat-

---

* To whom correspondence should be addressed. E-mail: fsbrisse@sympatico.ca.

[†] Université de Montréal.

[‡] Nankai University.

(1) (a) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447. (b) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703.

(2) (a) Withersby, M. A.; Blake, A. J.; Champness,N. R.; Cooke, P. A.; Hubberstey, P.; Li, W. S.; Shröder, M. *Inorg. Chem.* **1999**, *38*, 2259. (b) Blake, A. J.; Champness, N. R.; Cooke, P. A.; Nicolson, J. E. B.; Wilson, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3811.

(3) For example: (a) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Schröder, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2327. (b) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (c) Chatterton, N. P.; Goodgame, D. M. L.; Grachvogel, D. A.; Hussain, I.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2001**, *40*, 312.

(4) Bu, X. H.; Chen, W.; Hou, W. F.; Du, M.; Zhang, R. H.; Brisse, F. *Inorg. Chem.* **2002**, *41*, 3477.

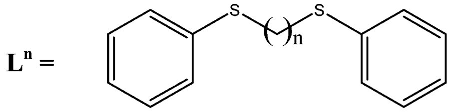
10.1021/ic051357c CCC: $33.50

ing ability of anions is also very important. An important question is whether the topology of a compound is determined primarily by the nature of the ligand or the coordinating character of the anion. To understand the influence of the anion, especially its coordinating ability, we have explored several anions of different size and coordination strength.[7] These may be classified as follows: spherical anions that are noncoordinating[8] or weakly coordinating (group 1: PF_6^-, SbF_6^-, ClO_4^-, BF_4^-), moderately coordinating sulfonate anions (group 2: *p*-TsO^-, $CF_3SO_3^-$), and coordinating perfluorocarboxylate anions (group 3: $CF_3CO_2^-$, $CF_3CF_2CO_2^-$, $CF_3CF_2CF_2CO_2^-$, $^-OOCF_2CF_2COO^-$). The planar NO_3^- anion is in a class by itself as it is small in size but fairly coordinating and potentially bidentate.

The structures of previously reported networks were found to be influenced by the nature of the counteranion, the metal-to-ligand ratio, the length (size) of the ligand, as well as the recrystallization solvent.[4,7] In a study of coordination networks based on bis(phenylthio)methane,[7a] 1D-coordination polymers were obtained regardless of the coordination strength of the anion. However, simple $[Ag-ligand-]_\infty$ polymeric chains were produced in the presence of weakly coordinating anions (BF_4^-, ClO_4^-). In these cases, the anions only complete the coordination sphere of Ag(I). When stronger anions were involved, three different types of double-stranded polymeric chains were noted. In these, both the anions and the ligands were involved in the formation of 1D-coordination polymers with Ag(I). A comparable distinction could be made with the slightly longer ligand, 1,3-bis(phenylthio)propane.[7b] The noncoordinating anions of group 1 were observed as guests in the $(Ag-ligand)_\infty$ layer structures. On the other hand, a variety of 2D-coordination networks that included all the structural units were observed for the medium and strongly coordinating anions of groups 2 and 3.

It has been noted on many occasions that chemically symmetrical molecules containing a central aliphatic segment with an even number of methylenes often have a crystallographic center of symmetry in the middle of the central CH_2-CH_2 bond. For example, the free ligands $\mathbf{L^4}$, $\mathbf{L^6}$, $\mathbf{L^8}$, and $\mathbf{L^{10}}$, which all contain an aliphatic sequence with an even number of CH_2 groups, are in the fully extended conformation.[9] Thus, we have extended our previous work by investigating supramolecular networks based on diarylthioether spacers with an even number of carbon atoms in the aliphatic part. Herein, we report the synthesis and characterization of a number of silver coordination polymers obtained by varying the counteranion as well as the length of the spacer. We previously reported that perfluorocarboxylate anions formed supramolecular networks containing weak Ag−Ag interactions[7] with bis(phenylthio)methane and 1,3-bis(phenylthio)propane building blocks. This present study was thus undertaken in order to identify new supramolecular architectures involving silver−silver short interactions. The building blocks used are depicted in Chart 1.

Chart 1



n = 2 : 1,2-bis(phenylthio)ethane ($\mathbf{L^2}$); n = 4 : 1,4-bis(phenylthio)butane ($\mathbf{L^4}$)

n = 6 : 1,6-bis(phenylthio)hexane ($\mathbf{L^6}$); n = 10 : 1,10-bis(phenylthio)decane ($\mathbf{L^{10}}$)

Experimental Section

Materials and General Methods. Except for the ligands, all of the reagents required for the syntheses were commercially available and employed without further purification. Elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). IR spectra were recorded on a Perkin-Elmer 1750 FTIR (4000−450 cm^{-1}) spectrometer with samples prepared as KBr pellets. ^1H (400 and 300 MHz) and ^{19}F (376.31 MHz) solution NMR spectra were recorded on Bruker AV400 and AV300 spectrometers at 25 °C. Chemical shifts are reported in parts per million and are referenced to tetramethylsilane (internal reference) for ^1H spectra. The chemical shifts are referenced to $C_6H_5CF_3$ (−63.9 ppm) for ^{19}F.

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

Syntheses. The ligands $\mathbf{L}^n$ ($n = 2, 4, 6, 10$) were synthesized according to the method previously reported in the literature,[10] and their characterizations are detailed in the Supporting Information section.

$[Ag_2L^2(CF_3SO_3)_2]_\infty$ (1). To a solution of $AgCF_3SO_3$ (265 mg, 1.031 mmol) in acetone (5 mL) was added a solution of $\mathbf{L^2}$ (109 mg, 0.442 mmol) in diethyl ether (5 mL). The reaction mixture was held at 50 °C for 90 min, then filtered while hot. The complex was recrystallized from a hot diethyl ether solution in a closed vessel stored in the dark. After a few days, single crystals suitable for X-ray analysis were obtained. Yield: 65% based on $AgCF_3SO_3$. Anal. Found: C, 25.61; H, 2.02. Calcd for $C_{16}H_{14}Ag_2F_6O_6S_4$: C, 25.28; H, 1.86. ^1H NMR (acetone-d_6, 300 MHz): δ 3.29 (s, 4H, $-S-(CH_2)_2-S-$), 7.41−7.63 (m, 10H, C_6H_5-). ^{19}F NMR (acetone-d_6, 376.31 MHz): δ −79.15. IR (KBr, cm^{-1}): 3442m, 3057w, 3003w, 2935w, 1611w, 1581m, 1510w, 1479m, 1428m, 1384w, 1254vs, 1178s, 1085w, 1070w, 1033s, 1000w, 906w, 829w, 769w, 735s, 715w, 690m, 652s, 643s, 577w, 517m, 488w, 477w.

$[Ag_2L^2(CF_3CO_2)_2]_\infty$ (2). The complex was synthesized in the same manner as **1** with $AgCF_3CO_2$ (232 mg, 1.05 mmol) and $\mathbf{L^2}$

---

(5) (a) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. (b) Turner, B.; Shterenberg, A.; Kapon, M.; Suwinska, K.; Eichen, Y. *Chem. Commun.* **2001**, 13. (c) Beer, P. D.; Gale, P. A.; *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (d) Gale, P. A. *Coord, Chem. Rev.* **2000**, *199*, 181.

(6) (a) Wu, H. P.; Janiak, C.; Rheinwald, G.; Lang, H. *J. Chem. Soc., Dalton Trans.* **1999**, 183. (b) Janiak, C.; Uehlin, L.; Wu, H. P.; Klüfers, P.; Piotrowski, H.; Scharmann, T. G. *J. Chem. Soc., Dalton Trans.* **1999**, 3121.

(7) (a) Awaleh, M. O.; Badia, A.; Brisse, F. *Cryst. Growth Des.*, **2005**, *5*, 1897. (b) Awaleh, M. O.; Badia, A.; Brisse, F. *Inorg. Chem.* **2005**, *44*, 7833.

(8) (a) Jung, O. S.; Kim, Y. J.; Lee, Y. A.; Park, K. M.; Lee, S. S. *Inorg. Chem.* **2003**, *42*, 844. (b) Jung, O. S.; Kim, Y. J.; Park, J. Y.; Choi, S. N. *J. Mol. Struct.* **2003**, *657*, 207.

(9) (a) Awaleh, M. O.; Badia, A.; Brisse, F. *Acta Crystallogr.* **2005**, *E61*, o2479. (b) Chen, W.; Hou, B. H.; Zhou, L. N.; Wang, J. K.; Li, H. *Acta Crystallogr.* **2005**, *E61*, o1890. (c) Awaleh, M. O.; Badia, A.; Brisse, F. *Acta Crystallogr.* **2005**, *E61*, o2476. (d) Awaleh, M. O.; Badia, A.; Brisse, F. *Acta Crystallogr.* **2005**, *E61*, o2473. (e) Chen, W.; Yin, Q.-X.; Xie, C.; Wang, J.-K.; Li, H. *Acta Crystallogr.* **2004**, *E60*, o2147.

(10) Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta* **1979**, *35*, 265.

(113 mg, 0.458 mmol). Yield: 40% based on $AgCF_3CO_2$. Anal. Found: C, 31.40; H, 2.29. Calcd for $C_{18}H_{14}Ag_2F_6O_4S_2$: C, 31.42; H, 2.05. ^1H NMR (acetone-d_6, 300 MHz): δ 3.31 (s, 4H, $-S-(C\mathbf{H}_2)_2-S-$), 7.39−7.69 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): δ −74.17. IR (KBr, cm^{-1}): 3438m, 3077w, 3056w, 2935w, 1661vs, 1580m, 1479m, 1436m, 1384w, 1331w, 1209s, 1136s, 1086w, 1024m, 894w, 840m, 807m, 734s, 725m, 690m, 578w, 517w, 477w.

$[Ag_4L^2_{2.5}(ClO_4)_4(CH_3COCH_3)_2]_\infty$ (3). The complex was synthesized in the same manner as **1** with $AgClO_4{\cdot}H_2O$ (202 mg, 0.896 mmol) and **L^2** (80 mg, 0.325 mmol). Yield: 71% based on $AgClO_4{\cdot}H_2O$. Anal. Found: C, 31.10; H, 3.07. Calcd for $C_{41}H_{47}Ag_4Cl_4O_{18}S_5$: C, 31.54; H, 3.03. ^1H NMR (DMSO-d_6, 300 MHz): δ 3.41 (s, 4H, $-S-(C\mathbf{H}_2)_2-S-$), 7.43−7.66 (m, 10H, $C_6\mathbf{H}_5-$). IR (KBr, cm^{-1}): 3435m, 3056w, 1709m, 1687m, 1580m, 1479m, 1439m, 1363m, 1262w,1207w, 1091br, 1023s, 916m, 734s, 690s, 626s, 477m.

$[AgL^4(CF_3SO_3)]_\infty$ (4). A solution of $AgCF_3SO_3$ (241 mg, 0.938 mmol) and **L^4** (134 mg, 0.488 mmol) in diethyl ether (20 mL) was kept under reflux for 90 min. The filtrate was allowed to slowly diffuse in petroleum ether in the dark to obtain colorless single crystals suitable for X-ray analysis. Yield: 63% based on $AgCF_3SO_3$. Anal. Found: C, 38.46; H, 3.62. Calcd for $C_{17}H_{18}AgF_3O_3S_3$: C, 38.42; H, 3.41. ^1H NMR (acetone-d_6, 300 MHz): δ 1.94 (qt, 4H, $-S-CH_2-(C\mathbf{H}_2)_2-CH_2-S-$), 3.21 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-S-$), 7.39−7.68 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): −79.07. IR (KBr, cm^{-1}): 3468w, 3057w 2994w 2941w, 2926w, 2861w, 2346w, 1978w, 1955w, 1869w, 1803w, 1734w, 1579w, 1452m, 1480m, 1440m, 1417w, 1384w, 1315m, 1257vs, 1220s, 1204s, 1151s, 1167s, 1113m, 1094m, 1070m, 1028, 916w, 875w, 759w, 730m, 746s, 730m, 713w, 705w, 688s, 629s, 573w, 515m, 493m.

$[Ag_2L^4_{0.5}(CF_3CO_2)_2]_\infty$ (5). This complex was synthesized in the same manner as **4** with $AgCF_3CO_2$ (259 mg, 1.172 mmol) and **L^4** (153 mg, 0.557 mmol). Yield: 38% based on $AgCF_3CO_2$. Anal. Found: C, 24.92; H, 1.65. Calcd for $C_{12}H_9Ag_2F_6O_4S_1$: C, 24.89; H, 1.57. ^1H NMR (acetone-d_6, 300 MHz): δ 1.87 (qt, 4H, $-S-CH_2-(C\mathbf{H}_2)_2-CH_2-S-$), 3.16 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-S-$), 7.29−7.59 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): δ −74.20. IR (KBr, cm^{-1}): 3447m, 3057w, 2947w, 2927w, 2854w, 1685vs, 1586w, 1479m, 1437m, 1384w, 1312w, 1208vs, 1136s, 1094w, 1071w, 1023w, 893w, 840w, 804w, 731s, 702, 689m, 481w, 461w.

$[Ag_2L^4(CF_3CF_2CO_2)_2]_\infty$ (6). Complex **6** was synthesized in the same manner as **4** with $AgCF_3CF_2CO_2$ (270 mg, 0.997 mmol) and **L^4** (209 mg, 0.761 mmol). Yield: 57% based on $AgCF_3CF_2CO_2$. Anal. Found: C, 32.19; H, 2.04. Calcd for $C_{22}H_{18}Ag_2F_{10}O_4S_2$: C, 32.37; H, 2.22. ^1H NMR (acetone-d_6, 300 MHz): δ 1.84 (qt, 4H, $-S-CH_2-(C\mathbf{H}_2)_2-CH_2-S-$), 3.09 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-S-$), 7.26−7.48 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): δ −84.04 ($C\mathbf{F}_3$), −119.27 ($CF_3C\mathbf{F}_2$). IR (KBr, cm^{-1}): 3441w, 3074w, 2947w, 2928w 2854w, 1679s, 1480w, 1413m, 1330s, 1213s, 1071w, 1032s, 874w, 818s, 779m, 732s, 688m, 646w, 586m, 541m, 518w, 496w, 460w.

$[Ag_2L^4(CF_3CF_2CF_2CO_2)_2]_\infty$ (7). The complex was synthesized in the same manner as **4** with $AgCF_3CF_2CF_2CO_2$ (226 mg, 0.704 mmol) and **L^4** (206 mg, 0.751 mmol). Yield: 67% based on $AgCF_3CF_2CF_2CO_2$. Anal. Found: C, 31.42; H, 2.38. Calcd for $C_{24}H_{18}S_2Ag_2F_{14}O_4$: C, 31.46; H, 1.98. ^1H NMR (acetone-d_6, 300 MHz): δ 1.85 (qt, 4H, $-S-CH_2-(C\mathbf{H}_2)_2-CH_2-S-$), 3.12 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-S-$), 7.27−7.55 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): δ −81.93($C\mathbf{F}_3$), −116.69 ($CF_3C\mathbf{F}_2CF_2$), −127.76 ($CF_3CF_2C\mathbf{F}_2$). IR (KBr, cm^{-1}): 3422m, 2928m, 1667vs, 1481m, 1440m, 1407w, 1339m, 1223vs, 1156w, 1117m, 1079w, 1024w, 963m, 931m, 810m, 742m, 731m, 717m, 689m, 643w, 527w, 482w.

$\{[Ag_2L^6(CF_3CO_2)_2.H_2O]{\cdot}H_2O\}_\infty$ (8). A 5 mL portion of chloroform was added to 124 mg (0.41 mmol) of **L^6**. To this mixture was added a solution of $AgCF_3CO_2$ (217 mg, 0.982 mmol) in acetone (5 mL). It was then heated at 60 °C for 140 min. After cooling, the resulting solution was layered on diethyl ether and then stored at room temperature in the dark. Several days later, colorless crystals appeared. Yield: 35% based on $AgCF_3CO_2$. Found: C, 33.84; H, 3.63. Calcd for $C_{22}H_{26}Ag_2F_6O_6S_2$: C, 33.86; H, 3.36. ^1H NMR (acetone-d_6, 400 MHz): δ 1.47 (qt, 4H, $-S-(CH_2)_2-(C\mathbf{H}_2)_2-(CH_2)_2-S-$), 1.65 (qt, 4H, $-S-CH_2-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-CH_2-S-$), 3.01 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_4-C\mathbf{H}_2-S-$), 7.18−7.42 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): −74.25. IR (KBr, cm^{-1}): 3450br, 3055w, 2934w, 1684vs, 1580w, 1478w, 1436m, 1383w, 1207s, 1136s, 1086w, 1024m, 841m, 804m, 735s, 690m, 477w.

$[Ag_2L^6(CF_3CF_2CO_2)_2]_\infty$ (9). The complex was synthesized in the same manner as **8** with $AgCF_3CF_2CO_2$ (231 mg, 0.853 mmol) and **L^6** (156 mg, 0.516 mmol). Yield: 68% based on $AgCF_3CF_2CO_2$. Anal. Found: C, 33.98; H, 2.67. Calcd for $C_{24}H_{22}Ag_2F_{10}O_4S_2$: C, 34.14; H, 2.63. ^1H NMR (acetone-d_6, 400 MHz): δ 1.47 (qt, 4H, $-S-(CH_2)_2-(C\mathbf{H}_2)_2-CCH_2)_2-S-$), 1.65 (qt, 4H, $-S-CH_2-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-CH_2-S-$), 3.03 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_4-C\mathbf{H}_2-S-$), 7.14−7.34 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): −84.01 ($C\mathbf{F}_3$), −119.45 ($CF_3C\mathbf{F}_2$). IR (KBr, cm^{-1}): 3459m, 3058w, 2943w, 2924m, 2853w, 1682vs, 1584w, 1480m, 1458w, 1438w, 1411m, 1320s, 1214s, 1164vs, 1091w, 1070w, 1030s, 893w, 820m, 780w, 732s, 703w, 689m, 587w, 540w, 480w.

$[AgL^6_{0.5}(CF_3CF_2CF_2CO_2)]_\infty$ (10). The complex was synthesized in the same manner as **8** but using $AgCF_3CF_2CF_2CO_2$ (265 mg, 0.826 mmol) and **L^6** (198 mg, 0.655 mmol). Yield: 79% based on $AgCF_3CF_2CF_2CO_2$. Anal. Found: C, 33.04; H, 2.62. Calcd for $C_{13}H_{11}AgF_7O_2S$: C, 33.07; H, 2.35. ^1H NMR (acetone-d_6, 400 MHz): δ 1.48 (qt, 4H, $-S-(CH_2)_2-(C\mathbf{H}_2)_2-(CH_2)_2-S-$), 1.69 (qt, 4H, $-S-CH_2-C\mathbf{H}_2-(CH_2)_2-C\mathbf{H}_2-CH_2-S-$), 3.02 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_4-C\mathbf{H}_2-S-$), 7.17−7.36 (m, 10H, $C_6\mathbf{H}_5-$). ^{19}F NMR (acetone-d_6, 376.31 MHz): −81.98 ($C\mathbf{F}_3$), −116.66 ($CF_3C\mathbf{F}_2CF_2$), −127.87 ($CF_3CF_2C\mathbf{F}_2$). IR (KBr, cm^{-1}): 3446m, 3058w, 2944w, 2925w, 2854w, 1683vs, 1584w, 1481m, 1458w, 1439w, 1407m, 1339m, 1221s, 1159w, 1118m, 1084m, 1023w, 968m, 933m, 812m, 741m, 731s, 720w, 688m, 649w, 593w, 527w, 481w.

$[AgL^{10}(NO_3)]_\infty$ (11). To a solution of $AgNO_3$ (252 mg, 1.483 mmol) in methanol (5 mL) was added a solution of **L^{10}** (361 mg, 1.001 mmol) in diethyl ether (5 mL). The mixture was heated at 50 °C for 120 min and then filtered. After cooling, the filtrate was recrystallized from diethyl ether at room temperature and kept in the dark. After a few days, crystals suitable for X-ray analysis were deposited. Yield: 65% based on $AgCF_3NO_3$. Anal. Found: C, 49.92; H, 5.43; N, 2.43. Calcd for $C_{22}H_{30}AgNO_3S_2$: C, 50.00; H, 5.72; N, 2.65. ^1H NMR (acetone-d_6, 400 MHz): δ 1.31 (m, 8H, $-S-(CH_2)_3-(C\mathbf{H}_2)_4-(CH_2)_3-S-$), 1.47 (qt, 4H, $-S-(CH_2)_2-C\mathbf{H}_2-(CH_2)_4-C\mathbf{H}_2-(CH_2)_2-S-$), 1.61(qt, 4H, $-S-CH_2-C\mathbf{H}_2-(CH_2)_6-C\mathbf{H}_2-CH_2-S-$), 3.01 (t, 4H, $-S-C\mathbf{H}_2-(CH_2)_8-C\mathbf{H}_2-S-$), 7.18−7.40 (m, 10H, $C_6\mathbf{H}_5-$). IR (KBr, cm^{-1}): 3435m, 2922s, 2851s, 1749w, 1630w, 1581w, 1480m, 1465m, 1438m, 1384s, 1352vs, 1333s, 1232w, 1155w, 1084w, 1067w, 1037w, 1025w, 998w, 892w, 881w, 764w, 743m, 733s, 687s, 498w, 477w, 465w.

X-ray Crystallography. Crystal Structure Determinations. X-ray diffracted intensities were measured on a Bruker AXS Platform diffractometer equipped with a SMART 2K CCD area

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

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{16}H_{14}Ag_2F_6O_6S_4$	$C_{18}H_{14}Ag_2F_6O_4S_2$	$C_{41}H_{47}Ag_4Cl_4O_{18}S_5$	$C_{17}H_{18}AgF_3O_3S_3$	$C_{12}H_9Ag_2F_6O_4S$	$C_{22}H_{18}Ag_2F_{10}O_4S_2$
mol wt	760.25	688.15	1561.37	531.36	578.99	816.22
cryst size (mm^3)	0.27 × 0.11 × 0.07	0.25 × 0.14 × 0.10	0.24 × 0.06 × 0.05	0.34 × 0.17 × 0.13	0.25 × 0.11 × 0.07	0.25 × 0.12 × 0.09
cryst system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	8.3209(1)	30.2872(3)	13.2480(2)	9.7996(2)	13.1732(2)	9.7118(5)
b (Å)	10.8072(1)	8.8790(1)	14.2262(2)	10.1521(2)	13.8286(2)	11.3140(6)
c (Å)	25.6612(3)	18.0509(2)	14.7858(3)	11.7852(2)	8.7495(1)	14.0734(6)
α (deg)	90	90	92.851(1)	78.469(1)	90	111.128(3)
β (deg)	96.494(1)	120.43	101.993	66.297(1)	92.608(1)	91.177(3)
γ (deg)	90	90	101.449	68.346(1)	90	107.772(3)
V (Å^3)	2292.79(4)	4185.74(8)	2659.54(8)	995.97(3)	1592.22(4)	1358.67(12)
Z	4	8	2	2	4	2
D(calcd) (g cm^{-3})	2.202	2.184	1.950	1.772	2.415	1.995
F(000)	1480	2672	1546	532	1108	796
T (K)	100(2)	100(2)	100(2)	220(2)	220(2)	220(2)
μ (mm^{-1})	17.882	17.616	15.927	11.457	21.771	13.914
θ_{max} (deg)	72.64	72.79	72.88	72.80	72.92	73.08
R1^a	0.0257	0.0457	0.0417	0.0320	0.0385	0.0450
$R_w{}^b$	0.0630	0.1225	0.1011	0.0843	0.1020	0.1144
R [$F^2 > 2\sigma(F^2)$]	0.0295	0.0468	0.0501	0.0352	0.0432	0.0569
wR (F^2)	0.0641	0.1236	0.1041	0.0892	0.1048	0.1280
S^c	1.003	1.130	1.000	1.078	1.000	0.973

	7	**8**	**9**	**10**	**11**
formula	$C_{24}H_{18}Ag_2F_{14}O_4S_2$	$C_{22}H_{22}Ag_2F_6O_4S_2.(H_2O)_2$	$C_{24}H_{22}Ag_2F_{10}O_4S_2$	$C_{13}H_{11}AgF_7O_2S$	$C_{22}H_{30}AgNO_3S_2$
mol wt	916.24	780.29	844.28	472.15	528.46
cryst size (mm^3)	0.22 × 0.15 × 0.06	0.23 × 0.16 × 0.06	0.43 × 0.09 × 0.07	0.13 × 0.07 × 0.02	0.12 × 0.08 × 0.04
cryst system	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.5464(1)	19.1312(2)	10.2786(1)	5.0167(3)	5.5556(1)
b (Å)	11.2508(2)	17.8749(2)	13.0241(1)	12.0797(5)	18.6523(4)
c (Å)	14.8801(2)	8.8084(1)	13.3040(1)	13.1304(5)	21.9144(5)
α (deg)	88.094(1)	90	116.366(1)	95.093(3)	90
β (deg)	81.725(1)	117.088(1)	111.193(1)	91.816(3)	90.723(2)
γ (deg)	70.387(1)	90	92.934(1)	98.354(3)	90
V (Å^3)	1489.60(4)	2681.78(5)	1439.23(2)	783.35(6)	2270.69(8)
Z	2	4	2	2	4
D(calcd) (g cm^{-3})	2.043	1.933	1.948	2.002	1.546
F(000)	892	1544	828	462	1088
T (K)	100 (2)	100 (2)	100(2)	100(2)	100(2)
μ (mm^{-1})	12.983	13.893	13.161	1.500	9.023
θ_{max} (deg)	72.96	72.83	72.97	26.12	72.81
R1^a	0.0535	0.0372	0.0359	0.0455	0.0454
$R_w{}^b$	0.1408	0.1013	0.0936	0.1135	0.1114
R [$F^2 > 2\sigma(F^2)$]	0.0598	0.0384	0.0370	0.0481	0.0575
wR (F^2)	0.1447	0.1028	0.0945	0.1157	0.1156
S^c	1.033	1.042	1.044	1.038	0.971

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

detector using monochromatic Cu Kα ($\lambda = 1.54178$ Å) radiation. The X-ray intensity data was processed with the program SAINT.[11] An empirical absorption correction, based on multiple measurements of equivalent reflections, was applied using the program SADABS.[12] The space group was confirmed by the XPREP[13] routine in the program SHELXTL.[14] The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques.[15] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions using a riding model and refined isotropically.

In complex **7**, one heptafluorobutyrate anion was found to be disordered. This anion was split over two sites with occupancies of 67% and 33%. The C−F and C−C distances in the major and minor entities of this anion were constrained to be equal (SADI[15]). 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[15]).

The trifluoro group of **8** was found to be in four different orientations in the ratio 38/28/20/14. The C−F distances were constrained to be equal, while the thermal parameters were constrained such that they kept the same values in each orientation. In addition, the OW(4) water molecule is split over two centrosymmetrically related nearby sites. The thermal parameters of the phenyl group of **L^6** in complex **10** were found to be high because of

---

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

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

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

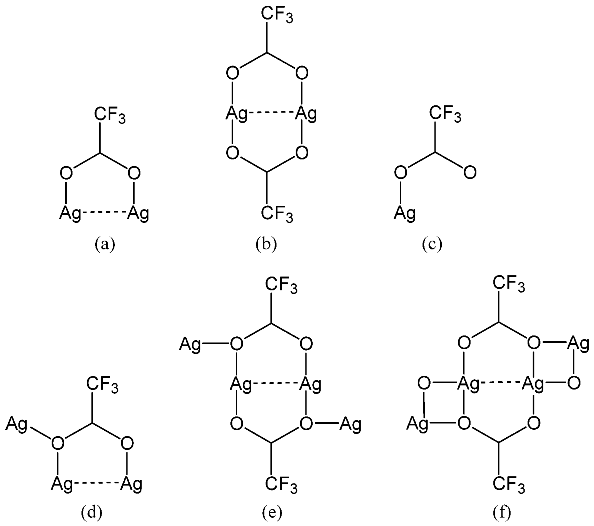
(14) *SHELXTL Release 5.10, The Complete Software Package for Single-Crystal Structure Determination*; Brucker AXS Inc.: Madison, WI, 1997.

(15) (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.

Table 2. Comparison of the Bond Distances (Å) Describing the Coordination of the Silver Atoms in Complexes **1**−**11**

1	Ag(1)−S: 2.482(1), 2.511(1); Ag(1)−O: 2.385(2)
	Ag(2)−S: 2.493(1), 2.526(1); Ag(2)−O: 2.372(2)
2	Ag(1)−S: 2.495(1), 2.834(1); Ag(1)−O: 2.279(3), 2.304(2); Ag(1)···Ag(1): 3.0813(5)
	Ag(2)−S: 2.498(1), 2.920(1); Ag(2)−O: 2.242(3), 2.304(3); Ag(2)···Ag(2): 3.3813(6)
3	Ag(1)−S: 2.625(1), 2.636(1), 2.642(1), 2.658(1)
	Ag(2)−S: 2.493(1), 2.507(1); Ag(2)−O: 2.549(4)
	Ag(3)−S: 2.493(1), 2.509 (1); Ag(3)−O: 2.538(4), 2.586(4)
	Ag(4)−O: 2.302(3), 2.350(4); Ag(4)−O: 2.476(4); Ag(4)−S: 2.452(1)
4	Ag−S: 2.475(1), 2.502(1); Ag−O: 2.323(2)
5	Ag(1)−S: 2.528(1), 2.589(1); Ag(1)−O: 2.346(3); Ag(1)···Ag(2): 3.3212(6)
	Ag(2)−O: 2.234(3), 2.271(3), 2.485(3); Ag(2)···Ag(2): 3.1688(7)
6	Ag(1)−S: 2.697(1); Ag(1)−O: 2.247(4), 2.334(4), 2.419(4); Ag(1)···Ag(2): 3.1048(6);
	Ag(1)···Ag(1): 2.9137(8); Ag(2)−O: 2.291(4); Ag(2)···Ag(1): 3.1048(6)
7	Ag(1)−S: 2.654(2); Ag(1)···Ag(1): 2.8669(9) Å; Ag(1)···Ag(2): 3.1594(6);
	Ag(1)−O: 2.268 (4), 2.359(4), 2.372(4)
	Ag(2)−O: 2.313(4); Ag(2)−S: 2.464(2), 2.525(2), 3.050(2); Ag(2)−Ag(1): 3.1594(6)
8	Ag−S: 2.534(1), 2.576(1); Ag−O: 2.496(4); Ag−OW(3): 2.417(2)
9	Ag(1)−O: 2.340(2), 2.352(2), 2.418(2); Ag(1)−S: 2.536(1); Ag(1)−Ag(1): 3.0052(4)
	Ag(2)−O: 2.419(2), 2.558(2); Ag(2)−S: 2.510(1), 2.549(1)
10	Ag−O: 2.256(3), 2.284(3); Ag−S: 2.644(1), 2.872(1); Ag−Ag: 2.9730(5)
11	Ag−O: 2.461(3), 2.491(3); Ag−S: 2.494(1), 2.512(1)

Scheme 1. Different Coordination Modes of the Perfluorocarboxylate Anions



disorder. Thus, the thermal displacement parameters of the phenyl group were restrained to be equal within an effective standard deviation and to not deviate much from a spherical shape (use of the DELU[15] and ISOR[15] instructions). Crystal data and data collection parameters are listed in Table 1.

Results

Crystal Structures. The bond distances describing the coordination of the silver atoms in complexes **1**−**11** are compared in Table 2.

[Ag$_2$L^2(CF$_3$SO$_3$)$_2$]$_\infty$ (1). The repeat unit of **1** consists of a 14-membered **Ag$_4$L$^2_2$S$_2$** macrocycle (Figure 1a). There are two crystallographically distinct silver atoms with comparable environments in the macrocycle. These silver atoms, Ag(1) and Ag(2), are associated via a μ_2-S bridge formed by the ligand, resulting in a polygonal mesh parallel to the (001)-plane (Figure 1b). The triflate is only a terminal coligand which completes the coordination sphere of the silver atoms (Figure 1a). The triflate, as well as the phenyl groups, is located on both sides of the corrugated layer (Figure 1c). Each silver atom, linked to two sulfur atoms from distinct ligands and to an oxygen from the triflate, adopts a deformed trigonal environment. The sum of the bond angles around Ag(1) and Ag(2) are 359.4° and 360.0°, respectively. In this complex, the 1,2-bis(phenylthio)ethane ligand is in the same trans conformation, S−C−C−S, −178.6(2)°, as the free ligand.[9a] In addition, the S···S distance in the ligand is 4.342 (1) Å, which is equivalent to that of the free ligand, 4.4312(7) Å.[9a]

[Ag$_2$L^2(CF$_3$CO$_2$)$_2$]$_\infty$ (2). Complex **2**, containing the trifluoroacetate anion, has two kinds of silver atoms: Ag(1) and Ag(2). Adjacent silver atoms of the same species are joined in a bridging fashion by two trifluoroacetate groups, thus giving rise to (Ag(1)O$_2$CCF$_3$)$_2$ and (Ag(2)O$_2$CCF$_3$)$_2$ dimers which are identical to those found in the structure of the trifluoroacetate silver salt[16] (Figure S1 and Scheme 1b).

Two consecutive dimers are connected, via a μ_2-S bridge, by **L^2** building blocks, thus generating a 2-D coordination network (Figure S2). The repeat unit of this complex is a 10-membered **Ag$_2$L$^2_2$** metallomacrocycle (Figure 2a and Figure S3a). The repeat units share their ligand edges and, in doing so, give rise to a ribbon parallel to the *b*-axis (Figure S3b). The ribbons are interconnected by silver−silver interactions, 3.0813(5) Å, of the (Ag(1)O$_2$CCF$_3$)$_2$ dimers so as to form a 2D-coordination network parallel to the *bc*-plane (Figure 2c and Figure S5).

In another description of the structure, there are two distinct repeat units in this complex, unit **A** and unit **B**.

In unit **A**, two silver atoms are linked by two ligands in order to form a 10-membered **Ag$_2$L$^2_2$** metallomacrocycle (Figure 2a and Figure S3a). The **A** units share their ligand edges, thus forming a ribbon parallel to the *b*-axis (Figure S3b). The **B** unit is formed by 10-membered **Ag$_6$S$_4$** metallomacrocycles (Figure 2b and Figure S4a). The units also share Ag···Ag edges in order to form a ribbon (Figure S4b). Alternating **A** and **B** ribbons share their silver and their sulfur atoms, resulting in a 2D-neutral sheet perpendicular to the *a*-axis (Figure 2c and Figure S5).

Each Ag(1) is linked to the sulfur atoms of two ligands, to two oxygen atoms from distinct trifluoroacetate groups,

---

[16] Griffin, R. G.; Ellett, J. D., Jr.; Mehring, M.; Bullitt, J. G.; Waugh, J. S. *J. Chem. Phys*, **1972**, *57*, 2147.

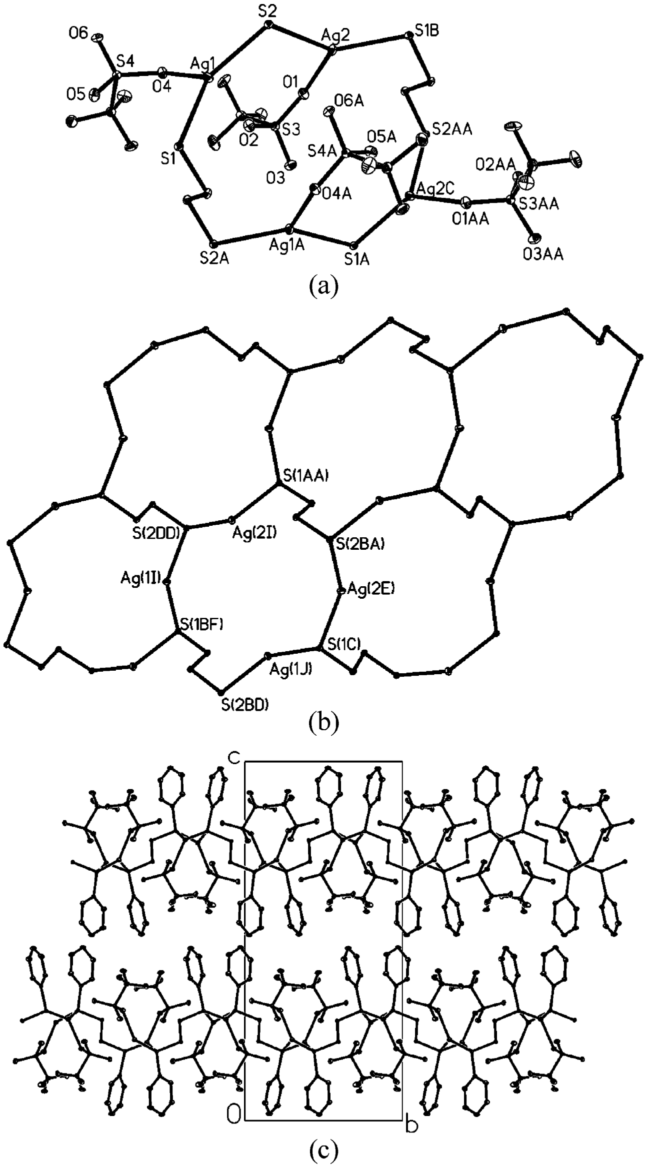


Figure 1. (a) The repeat unit of complex **1**, $\mathbf{Ag_4L^2{}_2S_2}$. (b) The 2D-network of **1** parallel to the (001)-plane (the phenyl groups and the hydrogen atoms are omitted for clarity). (c) In this packing of **1**, the layers are shown edge-on.

and to another silver atom producing a very distorted trigonal bipyramid. The other silver atom, Ag(2), has a tetrahedral coordination. It is surrounded by the sulfur atom of two ligands and is linked to two oxygen atoms from different trifluoroacetate groups. The Ag(2)···Ag(2) contact distance is 3.3813(6)Å, a distance slightly shorter than the sum of the van der Waals radius of two silver atoms, 3.44 Å.[17] The two Ag−S distances, 2.834(1) and 2.920(1) Å, are slightly longer than the "normal" silver−thiol distance. Such longer Ag−S distances are not unusual in Ag(I) complexes where the thiol is linked to adjacent silver atoms via a μ_2-S bridge. For example, Ag−S bonds of 2.912(5) and 2.959(5) Å are reported for the mercaptopyridine[18] and 2.936(2) Å in $[Ag_2(hfpd)_2([14]aneS_4)]_\infty$,[19] and 2.886 (1) Å for the *S*,*S*′-bis-(8-quinolyl)-4-oxa-1,7-dithiaheptane (OETQ).[20]

$\mathbf{[Ag_4L^2{}_{2.5}(ClO_4)_4(CH_3COCH_3)_2]_\infty}$ **(3).** In this complex, there are four types of silver atoms, Ag(1), Ag(2), Ag(3), and Ag(4), four perchlorate groups, and the ligand which is present in both the cis and the trans conformations. Two ligands in the cis conformation are connected to the Ag(1) silver atom in a chelating mode so as to form $\mathbf{AgL^2{}_2}$ (Ag(1)$\mathbf{L}^2{}_2$) metallomacrocycles. Each of the ligands' sulfur atoms are also bound to either Ag(2) or Ag(3). In doing so, chains of alternating $Ag(1)_2Ag(2)_2S_4$ and $Ag(1)_2Ag(3)_2S_4$ metallomacrocycles extending along the *c*-axis are obtained (Figure 3).

Two perchlorates complete the tetrahedral coordination of the Ag(3) atoms, while the coordination of Ag(2) is trigonal, with only one perchlorate group present. The chains, which run parallel to the *c*-axis, are associated in a 2D-coordination network with the help of the ligand in its trans conformation. The ligand thus binds two centrosymmetrically related Ag(4) atoms themselves bound to the oxygen of a perchlorate which, in turn, is coordinated to Ag(2). The other two ligands that complete the tetrahedral coordination of Ag(4) are the oxygen atoms of two acetone molecules. In other words, this perchlorate bridges Ag(2) and Ag(4) in a μ-O,O′ coordination mode. A 2D-network parallel to the (220)-plane is thus generated (Figure 3).

In terms of coordination, Ag(1) is connected to four sulfur atoms from two distinct ligands forming a distorted tetrahedral environment. Ag(2) is surrounded by three atoms in a trigonal arrangement: two sulfur atoms from different ligands and the oxygen atom of a perchlorate. This coordination is very distorted since the angles deviate strongly from 120°: S−Ag(2)−S, 153.7(1)°; S−Ag(2)−O, 102.1(1)° and 99.6(1)°, $\Sigma_{Ag} = 355.4°$. Ag(3) is tetrahedrally surrounded by two sulfur atoms from different ligands and by two oxygen atoms from distinct perchlorates. Finally, Ag(4) is surrounded by two oxygen atoms from acetone molecules, the oxygen atom from a perchlorate, and the sulfur atom from a ligand yielding a distorted tetrahedral coordination.

$\mathbf{[AgL^4(CF_3SO_3)]_\infty}$ **(4).** In its crystal structure, **4** forms a 1D-coordination polymer extending parallel to the [210]-direction. The succession of Ag(I) ions and ligands generates a zigzag [Ag−ligand−]$_\infty$ chain. The trigonal coordination of Ag(I) is completed by a trifluoromethanesulfonate anion. The sum of the bond angles around the silver atom is 359.9°. This 1D-chain can be considered as having a Y-shaped topology (Figure 4). From a crystallographic point of view, the silver atom is bound to two half ligands, the other half being generated by a crystallographic center of symmetry. Hence, there are two S···S separations with respective values of 6.944(1) and 6.915(1) Å.

Perfluorocarboxylates of L⁴. The three perfluororocarboxylates, $[\mathbf{Ag_2L^4{}_{0.5}(CF_3CO_2)_2}]_\infty$ (**5**), $[\mathbf{Ag_2L^4(CF_3CF_2CO_2)_2}]_\infty$ (**6**), and $[\mathbf{Ag_2L^4(CF_3CF_2CF_2CO_2)_2}]_\infty$ (**7**), are grouped under

---

(17) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*; Addison-Wesley: Reading, MA, 1984; pp168, 180.

(18) Hong, M.; Su, W.; Cao, R.; Zhang, W.; Lu, J. *Inorg. Chem.* **1999**, *38*, 600.

(19) Blake, A. J.; Champness, N. R.; Howdle, S. M.; Webb, P. B. *Inorg. Chem.* **2000**, *39*, 1035.

(20) Liao, S.; Su, C. Y.; Yeung, C. H.; Xu, A. W.; Zhang, H. X.; Liu, H. Q. *Inorg. Chem. Commun.* **2000**, *3*, 405.

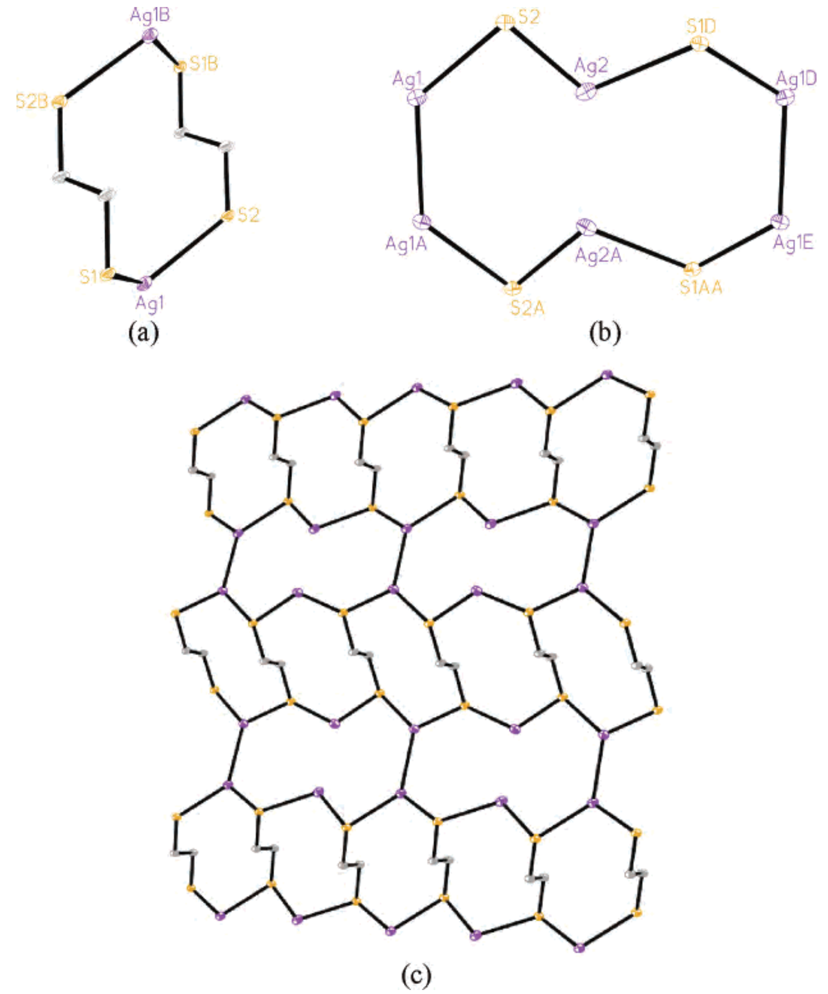


Figure 2. (a) The **A** repeat unit of complex **2**, **$Ag_2L^2_2$**. (b) The **B** repeat unit, **Ag_6S_4**. (c) The **A** units share their ligand edges forming a ribbon parallel to the *b*-axis. The **B** units share their Ag−Ag edges, giving rise to a ribbon alongside the *b*-axis. Neighboring **A** and **B** ribbons share their silvers as well as their sulfur atoms, resulting in a neutral 2D-network parallel to (100)-plane. The phenyl groups, the trifluoroacetate groups, and the hydrogen atoms are omitted for clarity.

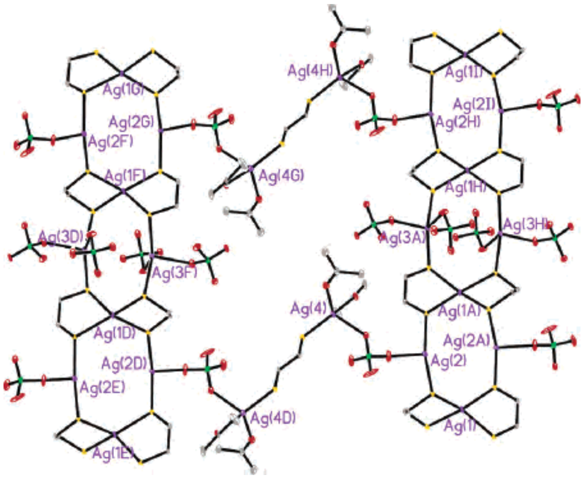


Figure 3. The four different silver atoms in **3**. The **$Ag_4L^2_4$** rings are interconnected and build a double-chain parallel to the *c*-axis. Adjacent double-chains form a 2D-coordination network through linkage with the ligand via the perchlorate anions. The resulting network is parallel to the (220)-plane. The phenyl groups and the hydrogen atoms are omitted for clarity.

this heading since it was observed that for the complexes with the 1,3-bis(phenylthio)propane ligand, increasing the length of the anion influenced the type of network adopted.[7b]

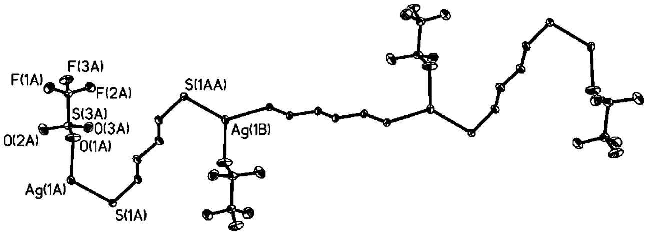


Figure 4. The 1D-coordination polymer of **4** extending alongside the [210]-direction. The anion is coordinated to the silver atoms. The phenyl groups and the hydrogen atoms are omitted for clarity.

Interestingly, the complexes all form centrosymmetric tetrameric units, although **5** has an Ag:L stoichiometry of 4:1 while both **6** and **7** have a 2:1 stoichiometry. The tetrameric units are compared in Figure 5.

There are two kinds of silver atoms in **5**: Ag(1) and Ag(2). Adjacent silver atoms, Ag(1) and Ag(2), are bridged by a trifluoroacetate group so as to form a dimer. Another trifluoroacetate group is bound to Ag(2) in a monatomic mode. A tetrameric unit, $(AgO_2CCF_3)_4$, results from a weak silver···silver interaction between Ag(2) atoms (Ag(2)···Ag(2): 3.1688(7) Å) (Figure 5a).

A 2-D network is generated by the coordination of one **L^4** ligand to four tetramers, via two μ_2-S bridges (Figure 6a

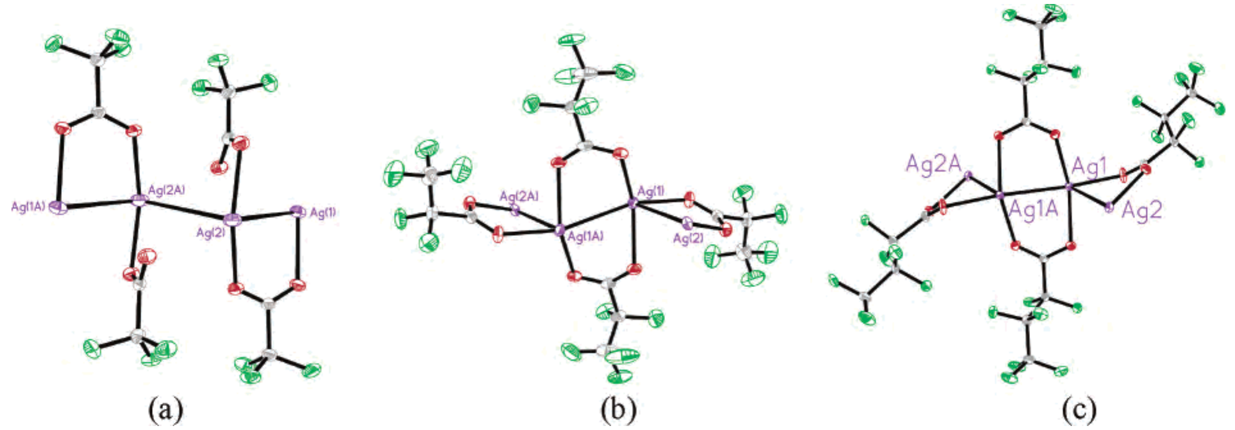


Figure 5. Comparison of the tetrameric units in the **L**^{4} complexes formed with (a) the trifluoroacetate anion, **5**; (b) the pentafluoropropionate anion, **6**; and (c) the heptafluorobutyrate anion, **7**.

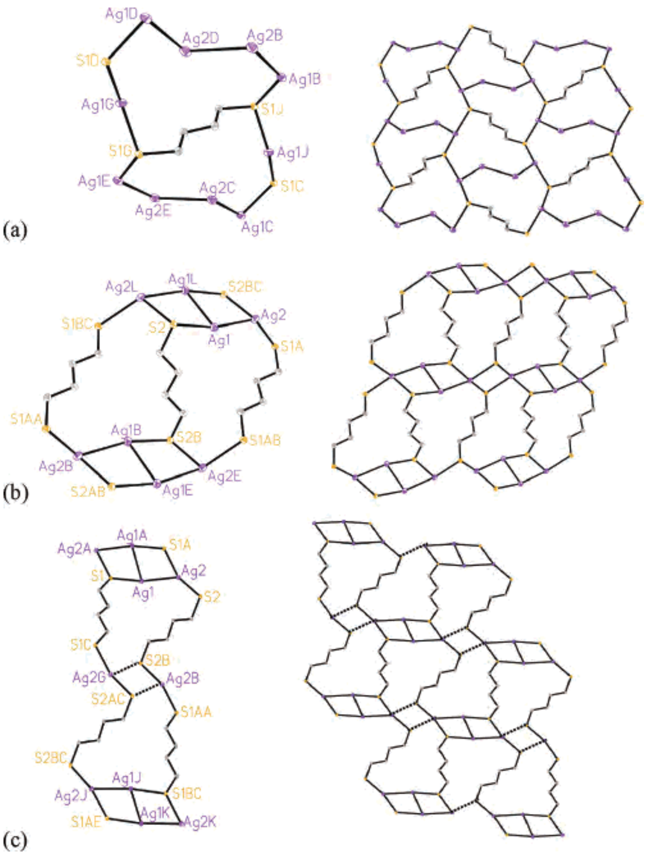


Figure 6. Comparison of the repeat units and the 2D-coordination networks in complexes formed with (a) the trifluoroacetate anion, **5**, in which the 2D-network is parallel to the (100)-plane; (b) the pentafluoropropionate anion **6**; (c) and the heptafluorobutyrate anion, **7**. The 2D-networks in both **6** and **7** are parallel to the (001)-plane. The anions, the phenyl groups, and the H atoms have been omitted for clarity.

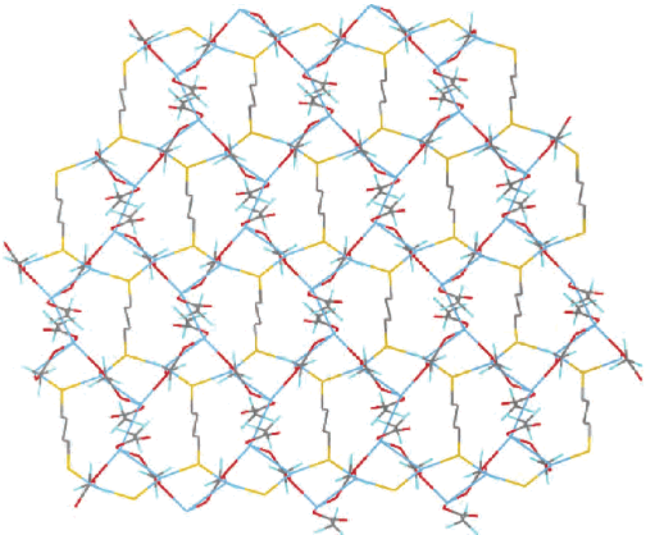


Figure 7. Projection of one layer of **5** revealing the two interconnected networks. The blue and red "diamond" network is that formed by the anions linked to the silver(I). The yellow and gray "hexagonal" network is formed by the **L**^{4} ligands and the silver(I) ions: gray, carbon atoms; yellow, sulfur atoms; blue, silver atoms; red, oxygen atoms.

and Figure S6). The repeat unit of this complex consists of two 12-membered subunits, **Ag$_5$L^{4}S**, sharing a ligand molecule. Both the central bond of the tetramer and that of the ligand are on crystallographic centers of symmetry.

Interestingly, this structure reveals the cooperation between the anions and the **L**^{4} ligand in the 2D-network formation (Figure S6). The projection of one layer of **5** (Figure 7) brings about the existence of two networks. One of them is made up of Ag(I) ions interconnected by the **L**^{4} ligands, while the other network is constituted of the same Ag(I) ions and the anions (Figure S6a,b). These two networks have the Ag(I) atoms in common, and **5** can be described equally well by emphasizing the role of the **L**^{4} ligand or that of the anions.

The tetrahedral coordination of Ag(1) in **5** consists of two sulfur atoms from two distinct ligands, an oxygen atom from a trifluoroacetate group, and Ag(2) with Ag(2)···Ag(1): 3.3212(6) Å. On the other hand, Ag(2) is coordinated to three oxygen atoms from three different trifluoroacetate groups, to Ag(2) (Ag(2)···Ag(2): 3.1688(7) Å) and to Ag(1). Hence, Ag(2) adopts a very distorted trigonal bipyramid.

The nearly identical complexes **6** and **7** contain two sorts of silver atoms. A bridged dimer is formed with two centrosymmetrically related Ag(1) atoms and two perfluorocarboxylate groups in a dibridging mode. In turn, each Ag(1) also forms a weak bond with another silver atom, Ag(2). This is reinforced by another perfluorocarboxylate monobridging Ag(1) and Ag(2). Hence, the $(AgO_2CCF_2CF_3)_4$ and $(AgO_2CCF_2CF_2CF_3)_4$ tetramers are formed in **6** and **7**, respectively (Figure 5b,c).

The tetramers are connected to each other by the **L**^{4} ligand, via μ_2-S bridges, producing neutral [Ag**L**^{4}(CF$_3$CF$_2$CO$_2$)]$_\infty$ and

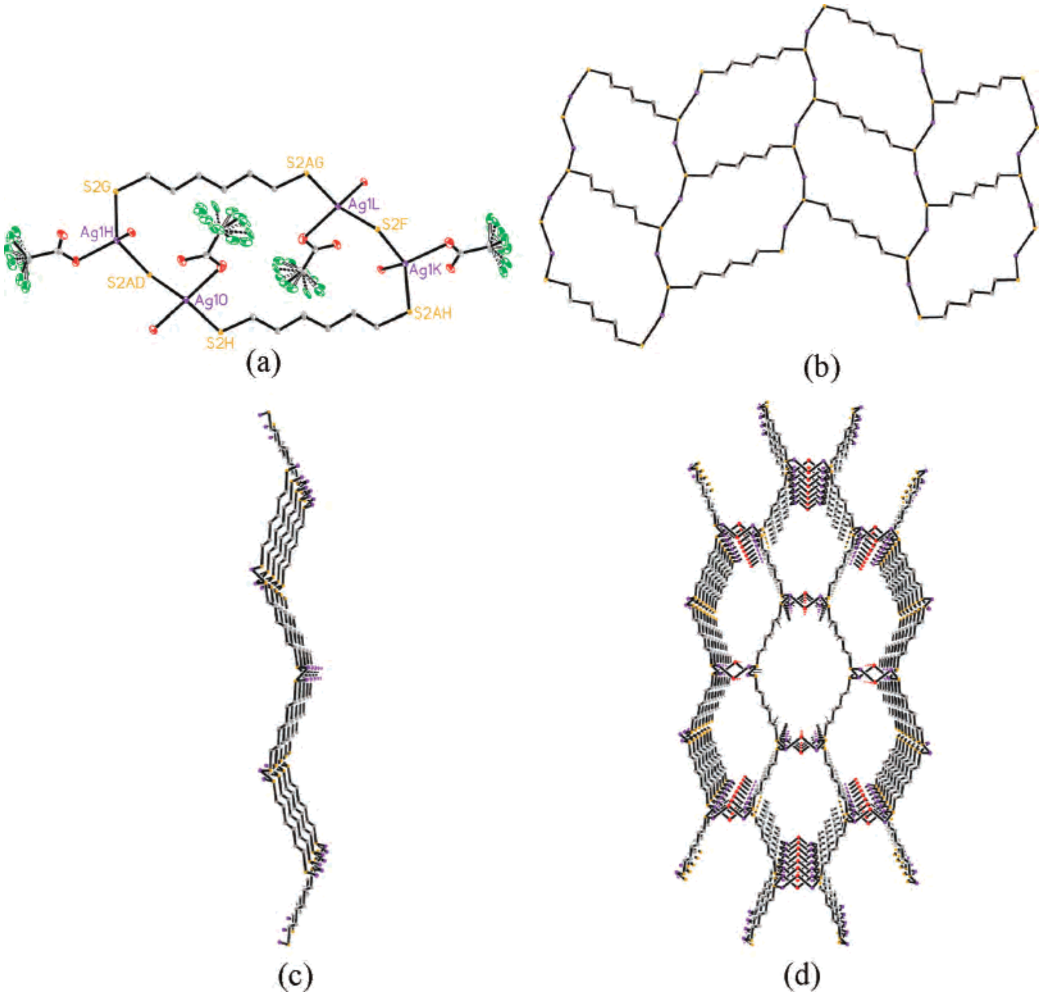


Figure 8. (a) The repeat unit of the 2D-network of **8**. The OW(4) water molecules, not shown, are located above and below the ring center. (b) One wavy sheet of **8**, parallel to the (100)-plane. The phenyl groups, the anions, and the hydrogen atoms have been omitted for clarity. (c) One sheet shown edge-on, i.e., at 90° from part b. (d) The 3D-network obtained when sheets of **8** are linked together by the oxygen atoms of water molecules. The phenyl and the trifluoroacetate groups, the water molecules inserted between the layers, as well as the hydrogen atoms have been omitted for clarity.

$[\mathrm{Ag}\mathbf{L}^{4}(\mathrm{CF_3CF_2CF_2CO_2})]_\infty$ layers perpendicular to the *c*-axis (Figure 6b,c). The repeat unit of these complexes may be described as two 15-membered $\mathbf{Ag_3L^4_2}$ macrocycles that share their ligand edges and four 4-membered, $\mathbf{Ag_3S}$ diamond-shaped ring.

The Ag(1) atom in **6** has an octahedral coordination: Ag(1) is linked to the sulfur atoms of a ligand, to three oxygen atoms of pentafluoropropionate groups, and to two adjacent silver atoms (Ag(1)···Ag(2): 3.1048(6) Å and Ag(1)···Ag(1): 2.9137(8) Å). On the other hand, the Ag(2) atom is connected to three sulfur atoms, to the oxygen atom of a pentafluoropropionate group, and to another silver atom (Ag(2)···Ag(1): 3.1048(6) Å). Therefore, Ag(2) has a distorted triangular bipyramid environment.

In complex **7**, adjacent Ag(1) atoms are dibridged by two heptafluorobutyrate groups, and at the same time each Ag(1) is connected to Ag(2) in a monobridging mode by one heptafluorobutyrate group in order to form a tetramer similar to that of **6** (Figure 5c). However, the $\mathbf{Ag_2S_2}$ diamond, shown by dotted lines in Figure 6c, has an Ag(2)−S* distance, 3.050(2) Å, clearly longer than in **6** (Figure 6c). Although it is at a rather long distance, this sulfur atom should be considered as being part of the environment of Ag(2), especially in view of the packing similarity between **6** and **7**. Exceptionally long Ag−S interactions, 3.0006(8) Å, have already been reported by Ahmed et al.[21] Thus, the Ag(1) silver atoms are octahedrally bound to one ligand, to one adjacent Ag(1) (Ag(1)···Ag(1): 2.8669(9) Å), to a neighboring Ag(2) (Ag(1)···Ag(2): 3.1594(6) Å), and to three oxygen atoms from three different heptafluorobutyrate groups. The other silver atom, Ag(2), is linked to an oxygen atom from an heptafluorobutyrate group, to two different ligands, to a more distant sulfur atom located at 3.050(2) Å, and to Ag(1), Ag(2)−Ag(1): 3.1594(6) Å. The coordination is that of a distorted trigonal bipyramid.

$\{[\mathbf{Ag_2L^6(CF_3CO_2)_2.H_2O].H_2O}\}_\infty$ **(8).** In complex **8**, which crystallizes with two water molecules, adjacent silver atoms are linked to the $\mathbf{L^6}$ building block in a μ_2-S bridging mode so as to form neutral sheets parallel to the (100)-plane (Figure 8b). The repeat unit of these layers is a 22-membered metallomacrocycle, $\mathbf{Ag_4L^6{}_2S_2}$ (Figure 8a). The trifluoroacetate group adopts a monodentate-coordinating mode and completes the coordination sphere of the silver atom (Scheme 1c). It is worth noting that, in this complex, there are two

---

(21) Ahmed, L. S.; Dilworth, J. R.; Miller, J. R.; Wheatley, N. *Inorg. Chim. Acta*. **1998**, *278*, 229 and references therein.

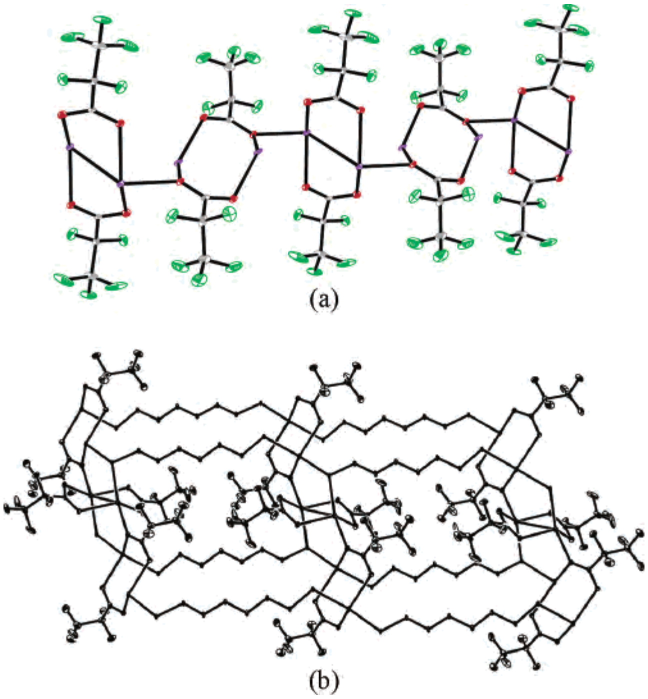


Figure 9. (a) A chain of **9** made up of a succession of dimeric units extending along the *a*-axis. Note that consecutive dimers are nearly at 90° to one another. (b) The 2D-coordination network of **9** parallel to the *ac*-plane. This layer is obtained as the ligands link the chains shown above. The hydrogen atoms and the phenyl groups have been omitted for clarity.

kinds of water molecules. The OW(3) water molecules, which are situated on a 2-fold axis of rotation, link two symmetrically related Ag atoms, and in doing so, build up a three-dimensional network (Figure 8c,d). The other water molecules, OW(4), are located between consecutive 22-membered metallomacrocycles (Figure S7). The 3D-network of **8** is constituted of diamondlike channels in which the phenyl groups of the spacer, as well as the trifluoroacetate anions, are located (Figure S7). In this complex, the silver atoms are tetrahedrally coordinated to two sulfur atoms from two distinct ligands, to an oxygen atom from a trifluoroacetate group, and to another oxygen from the OW(3) water molecule (Ag−OW(3): 2.417(2) Å).

[AgL^6(CF$_3$CF$_2$CO$_2$)]$_\infty$ (9). There are two kinds of silver atoms in complex **9**. Two neighboring Ag(1) atoms are connected in a diatomic bridging mode by two pentafluoropropionates group in order to form the (Ag(1)O$_2$CCF$_2$CF$_3$)$_2$ dimer in which the Ag(1)···Ag(1) distance is 3.0052(4) Å. A different dimer is formed with Ag(2) atoms, with a longer Ag(2)···Ag(2) distance of 3.3898(5) Å. Neighboring dimers, (Ag(1)O$_2$CCF$_2$CF$_3$)$_2$ and (Ag(2)O$_2$CCF$_2$CF$_3$)$_2$, which are almost orthogonal to one another (Φ: 89.6 (1)°), form a [Ag$_2$(O$_2$CCF$_2$CF$_3$)$_2$]$_\infty$ chain, via the oxygen atom of the pentafluoropropionate group, that extends parallel to the *a*-axis (Figure 9a). Adjacent chains are joined by the 1,6-bis(phenylthio)hexane, **L^6**, thus building a 2D-boxlike structure parallel to the (010)-plane (Figure 9b).

Each Ag(1) silver atom is linked to three oxygen atoms from distinct pentafluoropropionates, to a sulfur atom, and to an adjacent Ag(1) silver atom (Ag(1)−Ag(1): 3.0052(4) Å). Thus, Ag(1) has a distorted trigonal bipyramid coordination. By contrast, Ag(2) is coordinated to two oxygen atoms from different pentafluoropropionate groups, and to two sulfur atoms from different **L^6** ligands, resulting in a distorted tetrahedral coordination.

[AgL$^6_{0.5}$(CF$_3$CF$_2$CF$_2$CO$_2$)]$_\infty$ (10). Two centrosymmetrically related silver atoms are bound in a diatomic bridging mode by two heptafluorobutyrate anions, forming the (AgO$_2$CCF$_2$CF$_2$CF$_3$)$_2$ dimer. Dimers are linked to one another by the **L^6** building block, via a μ_2-S bridge, so as to build up a two-dimensional coordination network parallel to the (001)-plane (Figure 10). The repeat unit is an 18-membered metallomacrocycle, **Ag$_2$L$^6_2$**. Taking part in this large ring are two six-membered hexagonal rings, **Ag$_4$S$_2$** (Figure 10a). The phenyl and the heptafluorobutyrate groups occupy both sides of the layers (Figure 10b). The silver atom adopts a very distorted trigonal bipyramid environment. The silver atoms are connected to two oxygen atoms from distinct anions, to two sulfur atoms from different ligands, and to another silver atom (Ag−Ag: 2.9730(5) Å).

[AgL^{10}(NO$_3$)]$_\infty$ (11). To further study the influence of the length of the building block upon the networks, the 1,10-bis(phenylthio)decane ligand, **L^{10}**, was synthesized.[9d] In complex **11**, adjacent silver atoms are brought together by the nitrate anion which acts as a bidentate ligand. The result is a [Ag−NO$_3$−]$_\infty$ chain, parallel to the *a*-axis (Figure 11a). Adjacent chains are interconnected by the **L^{10}** ligand, resulting in a corrugated 2D-polymer network parallel to the (020)-plane (Figure 11b) as the **L^{10}** ligand is present in two distinct conformations. Although the two crystallographically

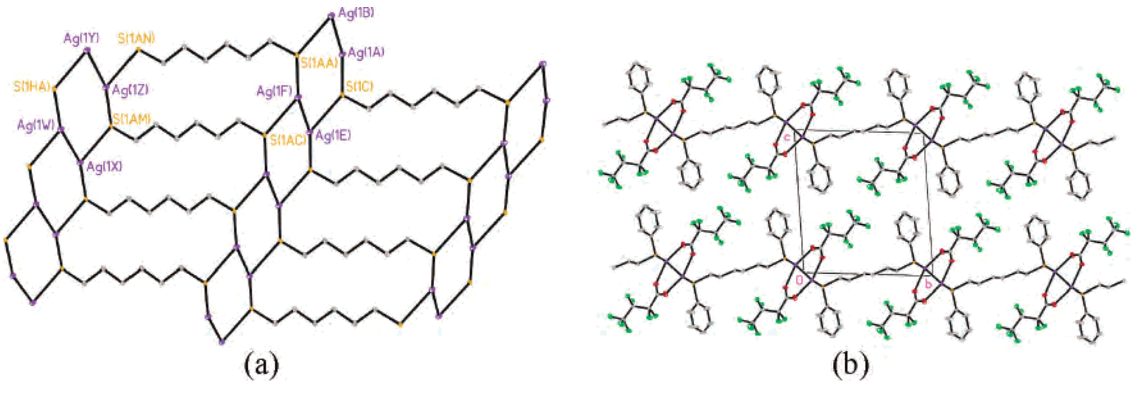
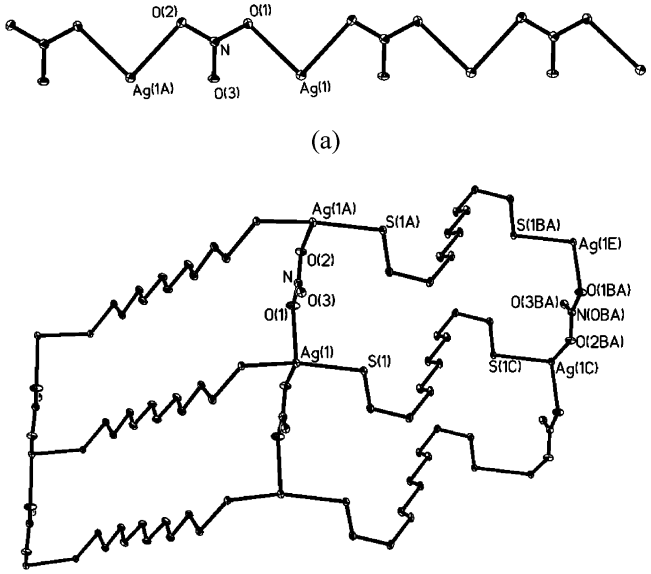


Figure 10. (a) The hexagonal **Ag$_4$S$_2$** rings are linked by the **L^6** ligands and yield the layer structure of **10** (the phenyl groups, the anions, and the H atoms have been omitted for clarity). (b) Projection on the *bc*-plane showing the packing of the layers. The H atoms are omitted for clarity.



(a)

(b)

Figure 11. (a) The 1D-coordination polymer of $[Ag-NO_3-]_\infty$ shown parallel to the *a*-axis. (b) Adjacent chains of $[Ag-NO_3-]_\infty$ are interconnected by the $\mathbf{L}^{10}$ ligand, thus forming a corrugated 2D-coordination network parallel to the (020)-plane. Note that the $\mathbf{L}^{10}$ connector adopts two distinct conformations. The hydrogen atoms and the phenyl groups have been omitted for clarity.

different $\mathbf{L}^{10}$ ligands each possesses a center of symmetry, one of them is in the completely extended conformation, while the other has the gauche−gauche−trans−trans conformation. It is the presence of these two gauche torsion angles that is responsible for the corrugated aspect of the 2D-layer.

In most of the structures reported herein, the ligand part of the complex sits on a crystallographic center of symmetry, and the ligand is usually in the fully extended conformation; that is, all the torsion angles along the aliphatic segment are trans. An aliphatic sequence containing an even number of methylene groups is usually centrosymmetric and adopts preferentially the trans conformation. For example, piperazinium 1-*n*-alkanecarboxylates[22a] or dibenzamido alkanes[22b] all contain aliphatic sequences which, when the number of CH_2 groups is even, these are centrosymmetric and adopt a fully extended conformation.

This is also true for the free ligands[9] $\mathbf{L}^4$, $\mathbf{L}^6$, $\mathbf{L}^8$, and $\mathbf{L}^{10}$. Thus, in the supramolecular architectures built with the ligands $\mathbf{L}^4$ and $\mathbf{L}^6$, it is not surprising to find that the ligands keep an all-trans conformation. In **11**, $\mathbf{L}^{10}$ has two conformations, an extended one and a gauche conformation. This prevents the structure from having large voids. The case of $\mathbf{L}^2$ is an interesting one since it is in the cis conformation and hence is chelated to Ag(I) in complex **3**, but adopts the trans conformation in **1**, **2**, and also **3**.

The repeat unit of **11** is a 34-membered metallomacrocycle. The silver atom is bound to two oxygen atoms from distinct nitrates, and to two sulfur atoms from different $\mathbf{L}^{10}$ building blocks, and has a slightly distorted tetrahedral coordination. Indeed, this complex is similar to that formed by the combination of $\mathbf{L}^4$ with the nitrate anion,[4] in which the neighboring silver atoms are linked through the nitrate in a μ-O,O′ coordination mode, thereby yielding a 1D-coordination polymer, $[Ag-NO_3-]_\infty$. The chains are linked by the $\mathbf{L}^4$ ligand thereby yielding a corrugated 2D-coordination network identical to that of complex **11**.

Infrared Spectroscopy. Infrared spectroscopy is usually used for the carboxylate moieties when X-ray structures are not available in order to differentiate the distinct coordination mode of the carboxylate groups, such as the bridging bidentate, chelating bidentate or unidentate modes on the

Table 3. Comparison of the COO^- Stretching Frequencie s (cm^{-1}) and SO_3^- Vibration Frequencies (cm^{-1}) Obtained by FTIR Spectroscopy

complex		$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_s(CO_2)$ (cm^{-1})	$[\nu_{as}(CO_2) - \nu_s(CO_2)]$ (cm^{-1})
2	$[Ag_2\mathbf{L}^2(CF_3CO_2)_2]$	1661	1384	277
5	$[Ag_2\mathbf{L}^4_{0.5}(CF_3CO_2)_2]$	1685	1384	301
6	$[Ag_2\mathbf{L}^4(CF_3CF_2CO_2)_2]$	1679	1413	266
7	$[Ag_2\mathbf{L}^4(CF_3CF_2CF_2CO_2)_2]$	1667	1407	260
8	$[Ag_2\mathbf{L}^6(CF_3CO_2)_2 \cdot 2H_2O]$	1684	1383	301
9	$[Ag_2\mathbf{L}^6(CF_3CF_2CO_2)_2]$	1682	1411	271
10	$[Ag\mathbf{L}^6_{0.5}(CF_3CF_2CF_2CO_2)]$	1683	1407	276
	$[Ag_2\mathbf{L}^3(CF_3COO)_2]^a$	1685	1410	275
	$[Ag_2\mathbf{L}^3(CF_3CF_2CO_2)_2(CH_3COCH_3)]^a$	1679	1411	268
	$[Ag\mathbf{L}^3(CF_3CF_2CF_2CO_2)]^a$	1681	1411	270
	$[Ag\mathbf{L}^1(CF_3CO_2)]^b$	1690	1390	300
	$[Ag\mathbf{L}^1(CF_3CF_2CF_2CO_2)]^b$	1682	1403	279
	$[Ag\mathbf{L}^1(OOCCF_2CF_2COO)]^b$	1683	1407	276
	$[Ag_2(CF_3COO)_2(dppm)]^c$	1670	1407	263
	$[Ag_2(CF_3CF_2COO)_2(dppm)]^c$	1672	1406	266
	$[Ag_2(CF_3CF_2CF_2COO)_2(dppm)]^c$	1670	1396	274

complex		$\nu_{as}(SO_3)$	$\nu_s(SO_3)$
1		1254	1033
4		1257	1033
	$[Ag\mathbf{L}^1(CF_3SO_3)]^a$	1258	1032
	$[Ag_2\mathbf{L}^1_2(CF_3SO_3)_2]^a$	1254	1027
	$[Ag_2\mathbf{L}^3(CF_3SO_3)_2(CH_3COCH_3)]^b$	1258	1033
	$[Ag_2\mathbf{L}^3(CF_3SO_3)_2]^b$	1260	1034
	$[Ag_2\mathbf{L}^3(CF_3SO_3)_2]^b$	1257	1030
	$[Ag_2\mathbf{L}(CF_3SO_3)_2]^d$	1257	1035

[a] Reference 7a· [b] Reference 7b. [c] Reference 28. [d] Reference 24 (**L**: dibenzo[*b*, *def*]chrysene).

basis of $\Delta\nu$ values ($\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2)$).[23] The bands observed at 1661 and 1384 cm^{-1} in the IR spectrum of complex **2** are assigned to the characteristic antisymmetric and symmetric stretching vibrations of the carboxylate group, respectively. Furthermore, the value of $\Delta\nu = [\nu_{as}(CO_2) - \nu_s(CO_2)]$, 277 cm^{-1}, obviously points to the occurrence of the dibridging mode,[24] in agreement with the established crystal structure. This observation applies also to **6**, **7**, **9**, and **10**, where the values of $\Delta\nu$ corroborate the X-ray results (Table 3a). The value of $\Delta\nu$ found for complex **8** (301 cm^{-1}) indicates the occurrence of the monatomic binding mode,[7a] as shown by the X-ray analysis of **8**. Although the crystal structure of **5** reveals the presence of both the diatomic-bridging mode and the monatomic-binding mode (Scheme 1a,c), only the latter is identified from its infrared spectrum, where the value of $\Delta\nu$ is 301 cm^{-1}.

The unambiguous assignment of the vibration modes of the $CF_3SO_3^-$ anion in complexes **1** and **4** is quite difficult because of the mixing of CF_3, SO_3, and organic ligand vibrations in the stretching-mode region between 1300 and 1000 cm^{-1}.[23,25] However, for the trifluoromethanesulfonate silver salt, as well as the coordination polymers containing the triflate, the absorption bands at 1270 and 1043 cm^{-1} have been assigned to the $\nu[SO_3(E)]$ and $\nu[SO_3(A_1)]$ vibrations.[25-27] The two absorption bands observed here for complexes **1** and **4**, listed in Table 3, are consistent with the triflate being coordinated to the silver atom.[7,28] The band at 1384 cm^{-1} for **11** is assigned to the $\nu_3(E')$ of the nitrate.[29] The perchlorate in complex **3** is present with two distinct coordination modes: unidentate (C_{3v}) and bridging bidentate (C_{2v}) (Figure 3). The observed absorption extending from 1041 to 1179 cm^{-1}, with a maximum at 1091 cm^{-1}, corresponds to assignments for both the C_{2v} and the C_{3v} symmetries.[30]

Discussion

I. Description and Topology of the Networks. The main reason for our interest in the role of the anions upon the topology is to synthesize materials with useful properties, such as molecular separation/recognition, especially anion-exchange and luminescence. In an earlier work, we reported that the structure of networks based on flexible diarylthioether building blocks and silver salts was influenced by the nature of the counteranion, the metal-to-ligand ratio, and the solvent used for recrystallization.[4,7] The difficulty in controlling all these factors is usually considered as the main reason for the lack of structure predictability. However, to gain more insight, we have investigated one at a time the effect of each parameter upon the topology of the networks formed. In this context, we have studied the role of the counteranion, which may be considered as a charged ligand, upon the structure of the resulting supramolecular networks when diarylthioether ligands are used as building blocks.[4,7] We explored the effect of the size and/or the coordination ability of several anions in the series PF_6^-, SbF_6^-, ClO_4^-, BF_4^-, NO_3^-, *p*-TsO$^-$, $CF_3SO_3^-$, $CF_3CO_2^-$, $CF_3CF_2CO_2^-$, $CF_3CF_2CF_2CO_2^-$, and $^-OOCF_2CF_2COO^-$.[7] The type of coordination network may be characterized on the basis of the role of the anion versus that of the ligand. We thus define a "ligand dominated" network by a structure where the silver and the ligand generate the structure and the anion only completes the coordination sphere of the metal center. The "anion-dominated" structures would be constituted of silver atoms and anions, while the ligand would have a secondary role. Finally, there are structures that could be described equally well by one or the other definition, in which neither the ligand nor the anion dominate. In this case, the silver atoms are part of two networks, $(Ag-anion)_\infty$ and $(Ag-ligand)_\infty$, which reinforce one another.

Influence of the Counteranions upon the Networks. In metal-organic crystal engineering, it has been reported that the type of anion has a strong influence upon the topology of the coordination networks.[31] In the same way, we reported that the supramolecular architecture of silver(I) salts with diarylthioether building blocks, such as **L^1** and **L^3**, is significantly influenced by the nature of the counteranions used.[7]

Group 1 counteranions usually act as templates and counter-balance the charge of the networks formed by the self-assembly of the silver(I) atom and the organic ligand.[7] Thus, we may consider that group 1 anions favor the formation of networks in which the organic spacer is indispensable. In other words, the organic ligand ensures the expansion of the networks, and the elements of group 1 counter-balance the charge of the networks or complete only the coordination sphere of the silver(I). We refer to this network as "ligand-dominated". For the complexes of the 1,3-bis(phenylthio)propane spacer, **L^3**, the noncoordinating anions allow for the formation of cationic layer structures, with a metal-to-ligand ratio 1:2 and in which the anions are inserted between the sheets.[7b] In addition, the bulk of the anions prevents the layers from getting too close to one another thus allowing for the presence of guest molecules between the cationic layers.[7b,32,33] The building block **L^5** reacted with Ag salts of XY_4^-, and XY_6^- also form cationic-layer networks,[34-36] similar to those obtained with **L^3**, with

---

[22] (a) Vanier, M. M.Sc. Thesis, Department of Chemistry, Université de Montréal, 1982. (b) Pineault, C. M.Sc. Thesis, Department of Chemistry, Université de Montréal, 1982.

[23] Effendy, N. C. D.; Nitiatmodjo, M.; Pettinari, C.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta*. **2005**, *358*, 735.

[24] Szlyk, E.; Szymanska, I.; Surdykowski, A.; Glowiak, T.; Wojtczak, A.; Golinski, A. *J. Chem. Soc., Dalton Trans.* **2003**, 3404 and references therein.

[25] Johnston, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 1045.

[26] Lawrance, G. A. *Chem. Rev*. **1986**, *86*, 17 and references therein.

[27] Batchelor, R. J.; Ruddick, J. N. R.; Sams, J. R.; Aubke, F. *Inorg. Chem*. **1977**, *16*, 1414 and references therein.

[28] Zhong, J. C.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Konaka, H. *Inorg. Chem.* **2001**, *40*, 3191.

[29] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-VCH: New York, 1978.

[30] Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331 and references therein.

[31] (a) Blake, A. J.; Champness, N. R.; Cooke, P. A.; Nicolson, J. E. B.; Wilson. C. *J. Chem. Soc., Dalton Trans.* **2000**, 3811. (b) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W. S.; Schroder, M. *Angew. Chem. Int. Ed.* **1997**, *36*, 2327.

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

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

a 1:2 metal-to-ligand ratio. There is also a report of a comparable 2D-coordination network when $\mathbf{L}^4$ is reacted with silver(I) perchlorate.[4] Hence, when the ligand is of an intermediate size ($\mathbf{L}^3$, $\mathbf{L}^4$, and $\mathbf{L}^5$), one obtains a 2D-coordination network that is “ligand-dominated”. Attempts to obtain comparable 2D-coordination networks with $\mathbf{L}^2$ or $\mathbf{L}^6$ were unsuccessful. So it seems that these structures are stable only when the ligand has an optimum dimension to form a relatively rigid network. For ligands larger than $\mathbf{L}^5$, the aliphatic segment is too flexible, i.e., it has too many torsion angles. For example, in the ClO_4^- complex of $\mathbf{L}^6$, the 1:1 metal-to-ligand ratio is preferred and a dinuclear unit (0D-structure) was reported by Bu et al.[38] In this structure, the perchlorate is coordinated to the silver atom. In the silver nitrate complex with $\mathbf{L}^{10}$ (**11**), where the NO_3^- anion has a bulk size comparable to that of BF_4^- or ClO_4^-, one finds that the ligand’s aliphatic segment is present in two different conformations, again showing an insufficient rigidity for the formation of 2D-cationic layer structures.

The perchlorate group is a particular case among the group 1 anions, in the sense that it sometimes coordinates to the silver atom as an unidentate ligand or acts as a bridging unit, as reported here for complex **3**. The perchlorate plays a non-negligible part in the construction of the network of **3**. Indeed, it is the bridging perchlorate which ensures the expansion of the network into a two-dimensional one (Figure 3). Thus, the question is “at what point can we consider a network as being ‘ligand-dominated’ or ‘anion-dominated’ and when do the neutral ligand and the charged ligand (anion) cooperate rather than compete for the construction of the coordination-networks?”

Sulfonates or Group 2 Anions. In this work, the multidentate trifluoromethanesulfonate does not take part in the network formation. In both complexes **1** and **4**, it merely completes the trigonal coordination of Ag(I) through one of its oxygen atoms. It was reported earlier[7a] that $CF_3SO_3^-$ acts with $\mathbf{L}^1$ as a single donor. However, in most other compounds, the sulfonate anions (*p*-TsO$^-$ or $CF_3SO_3^-$) act as bidentate ligands.[7a,b] The sulfonate anions seem to be ambivalent as to whether a 1D- or a 2D-coordination network is generated. It should be mentioned that these anions have the property of generating solvent-induced supramolecular polymorphism.[7a,b]

Perfluorocarboxylates or Group 3 Anions. These anions may adopt different coordination modes (Scheme 1). The perfluorocarboxylate which assumes a monodentate coordination mode, as in complex **8** (Figure 8a), is not considered necessary for the network formation since it only completes the coordination sphere of the silver atom. Hence, this network may be considered as “ligand-dominated”. A comparable situation is noted with $\mathbf{L}^1$ and the trifluoroacetate anion.[7a]

As expected, the bidentate perfluorocarboxylate anions form silver(I) dimers, as in the silver trifluoroacetate or the silver heptafluorobutyrate salts.[16,39] Less frequently, tetramers are also present (Figure 5a−c). In both cases, the group 3 anions are as necessary to the propagation of the networks as the neutral ligands, since the latter expand the dimers or the tetramers into networks (Figures 2, 6, 10). That is, both the anion and the neutral ligand are equally involved in the network; there is cooperation instead of competition between these structural units.

In addition, the oxygen atoms of the perfluorocarboxylate contain syn and anti lone pairs capable of coordinating to metal centers (Scheme 1d). It is worth pointing out that the structure of silver(I) trifluoroacetate is a 1D-polymeric chain consisting of interconnected dimers via the anti-lone pair of the oxygen atoms (Figure S9).[37] Group 3 anions may thus form 1D-coordination polymers or 2D-networks with the metal atoms (Figures 7, 9a). For example, in complex **9** with $\mathbf{L}^6$, one anti lone pair of one oxygen of the $(AgOOCCF_2CF_3)_2$ dimer is coordinated to the silver atom of an adjacent dimer in order to generate the 1D-coordination polymer $[Ag_2(CF_3CF_2CO_2)_2]_\infty$ (Figure 9a). These 1D-chains are linked to one another by the $\mathbf{L}^6$ spacer in order to create a 2D-network (Figure 9b). In this case, one observes that the neutral ligand, an organic building block, and the charged ligand, the perfluorocarboxylate, cooperate in order to form a 2D-network. In other words, when the charged ligand forms a one-dimensional coordination polymer with the silver atom, the ligand contributes to an increase in the dimensionality of the network.

In addition, a 1D-coordination polymer is formed when silver(I) tetrafluorosuccinate is reacted with $\mathbf{L}^1$.[7a] This chain has been described as a succession of pairs of silver atoms bridged at one end of the tetrafluorosuccinate anion and another pair of silver atoms bridged at the other end, and so on, thus forming a $[Ag_2{-}OOCCF_2CF_2COO{-}]_\infty$ ribbon (Figure S8a). However, in this case, the neutral ligand does not increase the dimensionality of the network, as expected, but only reinforces the $[Ag_2{-}OOCCF_2CF_2COO{-}]_\infty$ chain by linking consecutive silver atoms (Figure S8).

The perfluorocarboxylates in **5** form a two-dimensional structure with the silver atoms (Figure 7), which may be seen as consisting of two intertwined networks. Neither the ligand nor the anions seem to dominate (Figure S6).

The small nitrate group may easily approach the metal center so that it should be considered as fairly coordinating.[8] Since this charged ligand is a coordinating one, we can expect that it contributes to the construction of the network. With both $\mathbf{L}^4$ and $\mathbf{L}^{10}$, the nitrate anions link adjacent silver atoms in a μ-O,O′ mode resulting in the 1D-coordination polymer, $[Ag{-}NO_3{-}]_\infty$. These chains, in turn, are linked to each other by the building block (Figure 11).[4] However, with $\mathbf{L}^6$, the nitrate adopts a μ-O,O monatomic bridging mode that links

---

(34) Chen, W.; Du, M.; Zhang, R. H.; Bu, X. H. *Acta Crystallogr.* **2001**, *E57*, m213.

(35) Du, M.; Zhao, X. J. *Acta Crystallogr.* **2004**, *E60*, m193.

(36) Bu, X. H.; Hou, W. F.; Du, M.; Chen, W.; Zhang, R. H. *Cryst Growth Des.* **2002**, *2*, 303.

(37) Karpova, E. V.; Boltalin, A. I.; Korenev, Yu. M.; Troyanov, S. I. *Russ. J. Coord. Chem.* **1999**, *25*, 65.

(38) Chen, W.; Du, M.; Bu, X. H.; Zhang, R. H.; Mak, T. C. W. *Cryst. Eng. Commun.* **2003**, *5(20)*, 96.

(39) Blakeslee, A. E.; Hoard, J. L. *J. Am. Chem. Soc.* **1956**, *78*, 3029.

Table 4. Comparison of the Short Ag···Ag Contact Distances (Å) Observed Herein with Corresponding Values Reported for Similar Ligands

complex	ligand	anion	Ag···Ag contact	structural unit
	L^1[a]	$CF_3CF_2CF_2COO^-$	3.1593(3)	dimer
	L^1[a]	$^-OOCCF_2CF_2COO^-$	2.9836(5), 3.0168(5)	dimer
2	L^2	CF_3COO^-	3.0813(5), 3.3813(6)	dimer
	L^3[b]	CF_3COO^-	3.2459(5)	dimer
	L^3[b]	$CF_3CF_2COO^-$	3.0502(7)	dimer
	L^3[b]	$CF_3CF_2CF_2COO^-$	3.1594(4)	dimer
5	L^4	CF_3COO^-	3.1688(7), 3.3212(6)	tetramer
6	L^4	$CF_3CF_2COO^-$	2.9137(8), 3.1048(6)	tetramer
7	L^4	$CF_3CF_2CF_2COO^-$	2.8669(9), 3.1594(6)	tetramer
9	L^6	$CF_3CF_2COO^-$	3.0052(4), 3.3898(5)	dimer
10	L^6	$CF_3CF_2CF_2COO^-$	2.9730(5)	dimer

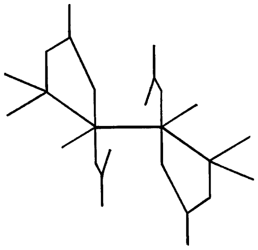
[a] Reference 7a. [b] Reference 7b.

adjacent silver atoms and gives rise to an **Ag_2O_2** ring. Neighboring rings are interconnected by the ligand so as to build a 2-D coordination network, that is different from that formed with the former ligands.[38]

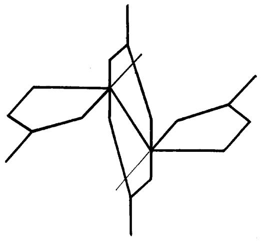
Thus, the coordination ability of the anions, charged ligands, plays a non-negligible role in the formation of the supramolecular architectures in metal−organic crystal engineering. However, the versatile coordination mode of coordinating anions, such as those of group 3 or the nitrate, limits the predictability of the structure of the networks formed with the silver atoms. It is worth noting that in all the perfluoroacetate-based networks[7] there are weak silver−silver interactions.

II. Silver−Silver Contacts. As expected, bidentate perfluorocarboxylate anions favor the formation of silver(I) dimers or tetramers (Scheme 1, Figure 5). Dimers are reported for the silver trifluoroacetate or the silver heptafluorobutyrate salts.[16,39] We have also observed these structures in networks based on the **L^1** and the **L^3** ligands with trifluoroacetate, pentafluoropropionate, heptafluorobutyrate, or tetrafluorosuccinate.[7] In all cases, two adjacent silver atoms are bonded together in a binuclear bridging mode by two perfluorocarboxylate groups in order to form $(AgOOCR)_2$ dimers ($R = CF_3$, CF_3CF_2, $CF_3CF_2CF_2$, or $OOCCF_2CF_2COO$). Consequently, weak silver−silver interactions occur between the silver atoms of the dimers. The observed Ag···Ag distances are listed in Table 4 and compared with those reported in other perfluorocarboxylate dimers. All these distances are shorter than the sum of the van der Waals radii of two silver atoms (3.40 Å[17]), and slightly longer than 2.89 Å, twice the radius of metallic silver,[17] indicating the presence of weak silver−silver interactions.[40,41]

Description of the Dimers. Dimers were observed in complexes **2**, **9**, and **10**. Complexes **2** and **9** have two crystallographically distinct $(AgOOCR)_2$ dimers which differ by the strength of the silver−silver interaction. There is always a short and a long Ag···Ag interaction, the longer distance being almost equal to the sum of the van der Waals radius of two silver atoms. In these cases, we believe that there are no interactions between the silver atoms. On the other hand, the short distances in **2**, **9**, and **10** are clearly less than the silver−silver separation of 3.16 Å observed for the trifluoroacetate-bridged silver−silver systems according to Bosch et al.,[40b] and points to a weak interaction between the silver atoms as described by Wang et al.[41a]



5 3.3212(6), 3.1688(7)



6 3.1048(6), 2.9137(8)
7 3.1594(6), 2.8669(9)

Figure 12. Schematic representation of the tetrameric units obtained with **L^4** and Ag−Ag distances (Å) in complexes **5**, **6**, and **7**. All three complexes are centrosymmetric.

Description of the Tetramers. It is of interest to note that tetramers are only observed with the **L^4** ligand. A schematic description of the two kinds of tetramers is illustrated in Figure 12. Complexes **6** and **7** are nearly identical, but differ significantly from **5**. All of the tetramers are centrosymmetric, and the silver atoms form a zigzag rather than a linear chain since all the Ag−Ag−Ag bond angles are in the range 96−99°. The Ag···Ag distances are all fairly short, and the central bond is always the shortest.

In **5**, the two extreme silver atoms are monobridged by one trifluoroacetate group, while a second ligand is attached to the central silver through one of its oxygens (Figure 12). There obviously must be a genuine Ag−Ag bond between the central atoms since these are not bridged by a trifluoroacetate. Thus, we think that the short distance between adjacent silver atoms may be attributed to weak silver−silver interactions rather than a geometrical restriction, especially since the central Ag···Ag distance is shorter than those between silver atoms held in a binuclear mode by one trifluoroacetate.

---

(40) (a) Powell, J.; Horvarth, M. J.; Lough, A.; Phillips, A.; Brunet, J. *J. Chem. Soc., Dalton Trans*. **1998**, 637. (b) Bosch, E.; Barnes, C. L. *Inorg. Chem*. **2001**, 2468. (c) Brammer, L.; Burgard, M. D.; Rodger, C. S.; Swearingen, J. K.; Rath, N. P. *Chem. Commun.,* **2002**, *4*, 239. (d) Brammer, L.; Burgard, M. D.; Eddleston, M. D.; Rodger, C. S.; Rath, N. P.; Adams, H. *Cryst. Eng. Commun*. **2002**, *4*, 239. (e) Brandys, M.-C.; Puddephatt, R. J. *J. Am. Chem. Soc*. **2002**, *124*, 3946.

(41) (a) Wang, Q. M.; Mak, T. C. W. *J. Am. Chem. Soc*. **2001**, *123*, 7594. (b) Ara, I.; Bahij, F.; Lachkar, M. *Acta Crystallogr*. **2003**, *C59*, m265.

Complexes **6** and **7** are nearly identical. The central silver atoms are dibridged by two perfluorocarboxylate ligands, while the extreme silver atoms are monobridged. The central Ag···Ag distances are among the shortest, these being almost equal to twice the radius of metallic silver or to the separation of silver atoms in silver metal, 2.89 Å.[17] Specifically, in **6**, the Ag1···Ag1 separation, 2.9137(8) Å, is merely 0.03 Å longer than the distance in silver metal,[17] indicating a moderate argentophilic interaction,[40] while the central bond in **7** is even shorter, with a value of 2.8669(9) Å.

Nevertheless, it is not clear how the electron-withdrawing power, due to an increase in the number of fluorine atoms in the counteranions, affects the coordination strength of the carboxylate groups, and consequently, the Ag···Ag interactions. On the other hand, such short Ag···Ag distances are not unusual in Ag(I) dinuclear complexes. For example, an Ag−Ag bond, 2.9710(4) Å long, has been reported for the trifluoroacetate groups bridging two silver cations in a 2:1 complex of bis(dimethylphenyl)pyrazine and silver(I) trifluoroacetate crystallized in acetonitrile and 3.1014(3) Å in the 2:2 complex crystallized in dichloromethane.[42] In the tetrafluorosuccinate silver acetylene diide,[43] the Ag−Ag distances are close to that in silver metal: in the crownlike [C2@Ag7] cage: they range from 2.8848(8) to 2.9526(8) Å. A longer distance of 3.116(1) Å is reported for Ag···Ag in the tetrameric silver thiolate phosphine complex.[21] Some Ag···Ag distances shorter than that found in metallic silver have been reported, for example, in diaquabis(betane) disilver(I) dinitrate (2.898(1) Å), and bis(pyridine betaine) disilver(I) diperchlorate,[47] (2.814(2) Å) or bis(3-hydroxyl-4-phenyl-2,2,3-trimethylcyclohexanecarboxylato) disilver(I) dihydrate [46] (2.778(5) Å).

In most coordination networks incorporating perfluorocarboxylate counteranions and flexible diarylthioether ligands, there are [Ag_2(carboxylate-*O*,*O*′)$_2$] dimers or [Ag_4(carboxylate-*O*,*O*′)$_4$] tetramers in which the Ag···Ag separation presents some argentophilicity,[44] which, according to Schmidbaur, may be regarded as an extension of the well-established concept of the aurophilicity for gold(I).[45]

Conclusions

Of the 11 complexes containing the 1,*n*-bis(phenylthio)-alkane ligands, $n = 2, 4, 6, 10$, and anions of different coordinating abilities, all but two complexes generate 2D-coordination networks. One (**4**) forms a 1D-coordination polymer while a 3D-network is noted for **8**, where water molecules join adjacent 2D-sheets.

The weakly coordinating anions (PF_6^-, SbF_6^-, ClO_4^-, BF_4^-) form layer structures with $\mathbf{L^3}$, $\mathbf{L^4}$, and $\mathbf{L^5}$ in which the anions are inserted within the layers. In the 1D-coordination polymers formed with Ag and $\mathbf{L^1}$, the anions are coordinated to the silver atoms. Here, we find that both the perchlorate and the nitrate groups act as bidentate anions. In **3**, ribbons made up of all three structural units are interconnected by the $\mathbf{L^2}$ ligand through two bidentate perchlorates, resulting in a very unusual 2D-network. The binding of silver atoms through the bidentate nitrate in **11** produces polymeric chains. These, in turn, are cross-linked through the $\mathbf{L^{10}}$ ligands, thus producing a 2D-coordination network.

Trifluoromethanesulfonate is a weak-to-medium coordinating anion, as with $\mathbf{L^1}$, or **1** (with $\mathbf{L^2}$) and **4** (with $\mathbf{L^4}$) it only completes the trigonal coordination of the metal.

The perfluorocarboxylates are strongly coordinated to the silver atoms, forming dimeric (**2**, **9**, **10**) or tetrameric units (**5**, **6**, **7**). It is of interest to note that the tetramers are obtained only with the $\mathbf{L^4}$ ligand. These units have a zigzag shape, since the Ag−Ag−Ag angles are close to 98°. The perfluorocarboxylates form dimeric units with $\mathbf{L^2}$ and $\mathbf{L^6}$. Both the dimers, and especially the tetramers, have very short metal−metal distances indicating the presence of weak silver···silver interactions.

Acknowledgment. This project was funded by the Natural Sciences and Engineering Research Council of Canada (F.B.). M.O.A. would like to thank the Programme Canadien de Bourse de la Francophonie for a scholarship. We also thank Dr. M. Simard and F. Bélanger-Gariépy for discussion, and H. Dinel for the elemental analyses.

Supporting Information Available: X-ray crystallographic information files (CIF) for compounds **1**−**11**. Details on the characterization of the ligands, table of bond distances and angles, and Figures S1−S9. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051357C

---

(42) Schultheiss, N.; Powell, D. R.; Bosch, E. *Inorg. Chem.* **2003**, *42*, 5304.
(43) Wang, Q. M.; Guo, G. C.; Mak, T. C. W. *J. Cluster Sci.* **2002**, *13*, 63.
(44) Zhang, X.; Guo, G. C.; Zheng, F. K.; Zhou, G. W.; Mao, J. G.; Dong, Z. C.; Huang, J. S.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **2002**, 1344−1349 and references therein.
(45) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391.
(46) Coggon, P.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1972**, 91.
(47) Chen, X. M.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1991**, 1219.