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One-Dimensional Coordination Polymers Incorporating Silver(I) Perfluorocarboxylate Cuboctahedral Clusters and the Bis(methylthio)methane Ligand

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Two topologically comparable complexes, $[Ag_6(CF_3CO_2)_3(L^{1-Me})_3(SCH_3)_3]_\infty$ (**1**) and $[Ag_6(CF_3CF_2CO_2)_3(L^{1-Me})_2(SCH_3)_3(H_2O)]_\infty$ (**2**), were prepared and characterized by single-crystal diffractometry. The structures consist of $Ag_{12}S_6$ clusters linked by bis(methylthio)methane ligands, L^{1-Me}, thus forming 1D coordination polymers. The 12 Ag atoms of the cluster are situated at the corners of a distorted cuboctahedron. The sulfur atoms of the six μ_4-SCH_3 entities occupy a position ~0.8 Å above the center of each of the square faces of the polyhedron. The cleavage of the C–S bond of some of the ligands occurs during the syntheses, producing the $^-SCH_3$ anions. The coordination of the silver atoms varies from 5 to 7. The Ag···Ag contacts range from 2.9250(5) to 3.3615(6) Å and from 2.961(1) to 3.380(1) Å for **1** and **2**, respectively. A polymeric ribbon is obtained when four ligands link a given cluster to two others. The chains of **1**, held only by van der Waals forces, pack in a hexagonal manner. The two water molecules in **2** ($Ag{-}OH_2 = 2.385(7)$ Å) are coordinated to silver atoms of the cluster. They are also strongly hydrogen bonded to the oxygen atoms of two pentafluoropropionate groups, one within the cluster (O···O = 2.741(1) Å), the other in an adjacent chain (O···O = 2.818(1) Å). The chains, thus H bonded to one another, generate a 2D coordination network.

Introduction

The synthesis and characterization of metal-organic frameworks (MOFs) has been an active research area since the discovery of the first coordination polymers in the mid-1990s.[1,2]

A remarkable feature of metal-organic compounds is that the properties of the metal-inorganic center can be expanded using the organic building block. Hence, interest in the hybrid inorganic−organic extended solid state resides in the fact that its new physical properties, such as gas storage,[3] anion exchange,[4] nonlinear optics,[5] or magnetism[6] often differ from those of the parent organic or inorganic compounds. Because to some extent it is possible to design an organic connector in which the connecting sites have good coordinating abilities

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with the chosen metal, one may be able to tailor the physical properties of the resulting coordination polymer materials. However, even if the major goal in crystal engineering is to predict the resulting MOFs of a given system,[7] there still remains a long way to go before the synthesis of coordination polymers with predictable topologies is achieved because it is difficult to control the many factors that influence the crystallization process simultaneously.[8]

We are currently using flexible symmetrical dithioether ligands as organic building blocks to propagate the coordination sphere of the d^{10} metal centers, Ag(I) and Au(I), via metal-directed self-assembly[9] to investigate the influence of experimental parameters, such as the type of anions, the size and shape of the organic connectors, the metal-to-ligand ratio, and the recrystallization solvent among others, upon the supramolecular architectures.[10,11] It has been reported that the silver(I) centers have a propensity to form metallomacrocycle clusters when they are combined with asymmetrical thiol ligands as opposed to gold(I), which favors supramolecular arrangements.[9] However, the flexible symmetrical thioether spacers promote supramolecular arrangements for Ag(I) from 1D to 3D coordination polymers/networks that are formed in which the metal centers are propagated by the organic ligands.[10−15] In the gold(I) complexes, the Au(I)−Au(I) aurophilic interaction[16−22] allows for the expansion of the discrete molecules into 1D or 2D networks.[12]

We recently reported MOFs based on the self-assembly of the small bis(methylthio)methane, L^{1-Me}, building block and silver(I) salts, in which the anions have a marked influence upon the resulting coordination polymers or networks.[11] The combination of trifluoroacetate or heptafluorobutyrate and L^{1-Me} led to the formation of "isostructural" 2D frameworks in which the anions complete the coordination sphere of the silver(I) centers. Hence, the self-assembly of L^{1-Me} with pentafluoropropionate, an anion of intermediate size, was expected to be isostructural. Surprisingly, this latter complex was found to form a 1D coordination polymer consisting of ligand-linked clusters rather than the expected structure.

We serendipitously obtained another cluster-bearing structure when this small ligand was combined with silver(I) trifluoroacetate. However, no cluster could be obtained with the longer heptafluorobutyrate. Here, we report the structures of two unusual atlas-sphere dithioether silver clusters, $[Ag_6(CF_3CO_2)_3(L^{1-Me})_3(SCH_3)_3]_\infty$ (**1**) and $[Ag_6(CF_3CF_2CO_2)_3(L^{1-Me})_2(SCH_3)_3\ (H_2O)]_\infty$ (**2**).

Experimental Section

Materials and General Methods. The ligand L^{1-Me} was synthesized following a published report.[23] The 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 solid samples prepared as KBr pellets for the complexes, and NaCl plates were used for the liquid ligand. The ^1H (300 MHz) NMR spectra in solution were recorded on a Bruker AV300 at 25 °C. Chemical shifts are reported in ppm and are referenced to tetramethylsilane as the internal reference for the ^1H spectra. No NMR spectra are reported for **1** and **2** because these complexes could not be solubilized. The GC/MS analyses were made on an Agilent Technologies 6890 Network GC system equipped with an HP-5MS capillary column and a 5973 MS selective detector. Melting points were obtained with a MEL-TEMP apparatus and are uncorrected.

Syntheses. $[Ag_6(CF_3CO_2)_3(L^{1-Me})_3(SCH_3)_3]_\infty$ (1). $Ag(CF_3CO_2)$ (217.2 mg, 0.98 mmol) was dissolved in acetone (5 mL). This mixture was stirred with a solution of bis(methylthio)methane (0.3 mL, 2.935 mmol) in diethyl ether (5 mL) at room temperature for 2 h and then filtered. The filtrate was left standing at room temperature for several months until single crystals suitable for X-ray analysis appeared (yield 32%). Anal. Found: C, 14.61; H, 2.31; calcd for $C_{18}H_{33}O_6F_9S_9Ag_6$: C, 14.89; H, 2.29. mp = 122 °C. IR (KBr, cm^{-1}): 3430 (w), 3047 (w), 2997 (w), 2924 (w), 2834 (w), 1678 (vs), 1411 (s), 1330 (vs), 1206 (vs), 1158 (vs), 1029 (s), 980 (w), 836 (w), 817 (s), 778 (w), 731 (s), 693 (w), 651 (w), 585 (m), 539 (w), 515 (w).

$[Ag_6(CF_3CF_2CO_2)_3(L^{1-Me})_2(SCH_3)_3(H_2O)]_\infty$ (2). This complex was synthesized in the same manner as **1** using $Ag(CF_3CF_2CO_2)$ (350 mg, 1.292 mmol) and L^{1-Me} (0.3 mL, 2.935 mmol). About 4 months later, single crystals suitable for X-ray analysis were deposited (yield 37%). Anal. Found: C, 14.62; H, 2.11; calcd for $C_{18}H_{27}O_7F_{15}S_7Ag_6$: C, 14.30; H, 1.80. mp = 126 °C. IR (KBr, cm^{-1}): 3431 (br), 3098 (w), 2916 (w), 2863 (w), 1670 (vs), 1437 (s), 1370 (m), 1323 (w), 1218 (vs), 1148 (vs), 840 (s), 807 (s), 725 (s), 598 (m), 516 (m).

X-ray Diffraction. The X-ray intensity data were collected on a SMART 6K CCD equipped with a rotating anode (Cu Kα, λ = 1.54178 Å) and an area detector using a Mirror Montel 200 Optics monochromator. The unit-cell refinement and data reduction were obtained with the program SAINT.[24] An empirical absorption correction, based on multiple measurements of equivalent reflec-

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

	1	2
formula	$C_{18}H_{33}Ag_6F_9O_6S_9$	$C_{18}H_{27}Ag_6F_{15}O_7S_7$
mol wt	1452.20	1512.02
cryst size (mm)	0.16 × 0.04 × 0.04	0.20 × 0.11 × 0.08
space group	$P2_1/c$	$P\bar{1}$
a (Å)	13.2763(2)	13.0172(8)
b (Å)	20.7631(4)	13.2443(8)
c (Å)	15.7275(3)	14.9673(9)
α (deg)	90	87.15(1)
β (deg)	109.47(1)	64.59(1)
γ (deg)	90	63.44(1)
vol (Å^3)	4087.41(13)	2052.3(2)
Z	4	2
D (calcd, g cm^{-3})	2.360	2.443
F(000)	2784	1436
temp (K)	200(2)	153(2)
μ(Mo Kα) (mm^{-1})	27.585	26.820
θ_{max} (deg)	68.96	68.88
$R^a[I \geq 2\sigma(I)]$	0.0351	0.0507
$R_w{}^b[I \geq 2\sigma(I)]$	0.0928	0.1249
R (all data)	0.0374	0.0865
R_w (all data)	0.0942	0.1466
S^c	1.040	0.944

[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] $S = [\sum w(F_o{}^2 - F_c{}^2)^2/(m - n)]^{1/2}$ (m is the number of reflections and n is the number of parameters).

tions, was applied using the program SADABS.[25] The space groups were confirmed by the XPREP[26] routine in the program SHELX-TL.[27] The structures were solved by direct methods and difference Fourier techniques with SHELXS-97.[28] The structure refinements were carried out on the basis of F^2 by full-matrix least squares. In **1**, two trifluoroacetate groups were found to be disordered over three different orientations in the ratios 40/36/24 and 60/20/20. The C−F distances of those anions were constrained to be equal (SADI).[28] The thermal parameters of all of the disordered atoms were constrained such that the corresponding atoms of the major and minor entities kept the same values (EADP).[28] In **2**, some of the CF_3 groups were slightly disordered because their thermal ellipsoids were larger than those of the other atoms. These atoms were constrained such that they had approximately the same thermal ellipsoids as the corresponding nondisordered atoms using the EADP instruction of SHELXS-97.[28] The H atoms on the water molecule of **2** were found on a Fourier difference map and were included in the refinement at their fixed positions. Crystal data and data collection parameters are listed in Table 1.

Results and Discussion

Crystals of complexes of **1** and **2** are quite difficult to obtain. It usually takes 4 to 5 months to grow them as small single crystals. These cannot be recrystallized because they cannot be redissolved. It is worth mentioning that **1** has a polymorph. However, it does not coexist, at the time of crystallization, with its other form.

$[Ag_6(CF_3CO_2)_3(L^{1-Me})_3(SCH_3)_3]$ (1). The content of the asymmetric unit and the atomic numbering of **1** are shown in Figure 1a. In this structure, the two centrosymmetrically related units generate a 12-silver nuclear complex, $[Ag_{12}(CF_3CO_2)_6(L^{1-Me})_6(SCH_3)_6]$, which may be best described as an atlas-sphere cluster (Figure 1b). These clusters are linked through the bis(methylthio)methane spacers and form a 1D coordination polymer.

The structural analysis reveals the presence of the $^-SCH_3$ entity that links four silver(I) ions in a μ_4-bridging mode (Figure 1b). This type of bridging is not unusual. For example, Su et al. reported a 1D coordination polymer where the $^-SC_2H_4NH_3{}^+$ zwitterion demonstrated the μ_4-bridging mode connecting four Ag(I) centers.[29] Similarly, Jeannin et al. reported that the action of an alkylthioalkyne on iron carbonyl produced a cluster containing the μ-SC_2H_5 entity.[30]

In the cluster of **1**, there are two types of sulfur atoms, each type being associated with a distinct coordination mode. The sulfur atom of the bis(methylthio)methane building block, L^{1-Me}, is coordinated to only one silver center, whereas the S atom of the $^-SCH_3$ unit is involved in four coordinations to Ag(I) atoms in a square-pyramidal configuration, $Ag_4(\mu_4\text{-}SCH_3)$.

The cluster may be described as being made up of three sections: a central layer consisting of an almost planar ring of eight atoms $(Ag{-}S{-})_4$, which has above and below it two square-based pyramids, $Ag_4(\mu_4\text{-}SCH_3)$. These pyramids are connected to the central eight-membered ring through Ag−Ag and Ag−S bonds. This description applies to any pair of diametrically opposed $^-SCH_3$ groups (Figure 1b).

Alternatively, the clusters may be described in terms of a distorted cuboctahedron. The notation 3^24^2 describing a perfect cuboctahedron indicates that two triangular faces and two square faces meet at each corner. The silver atoms occupy the corners of the polyhedron, whereas the sulphur atoms of the μ_4-SCH_3 units are located above each of the square faces (Scheme 1).

The 1D coordination polymer is obtained as each bis(methylthio)methane spacer joins the Ag(1) and Ag(5) atoms of the adjacent clusters (Figure 2).

The Ag−S distances, ranging from 2.605(1) to 2.656(1) Å, are in the normal interval for silver dithioether complexes (2.434(2)−2.697(1) Å) (Table S3).[11,31] The Ag−S distances for the μ_4-SCH_3 unit are shorter because they vary from 2.466(1) to 2.581(1) Å and are in the normal range for $Ag_4(\mu_4\text{-}SR)$.[29,30,32] The trifluoroacetate anions adopt two coordination modes (Figure 1a). In one case, the anion completes the coordination sphere of the metal center (Scheme 2a), and in the other, it bridges two silver atoms, resulting in the Ag(2)−O(3)−C(5)−O(4)−Ag(3) five-membered ring (Scheme 2b).

The bis(methylthio)methane organic connector plays two distinct roles. First, one L^{1-Me} bridges two silver(I) centers

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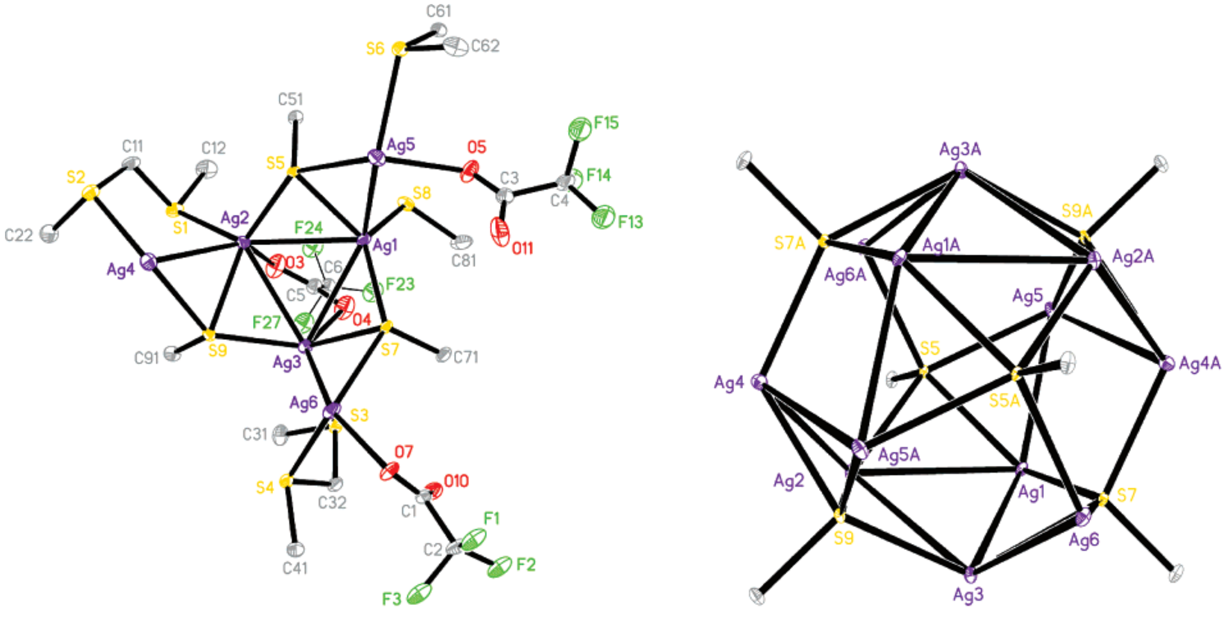
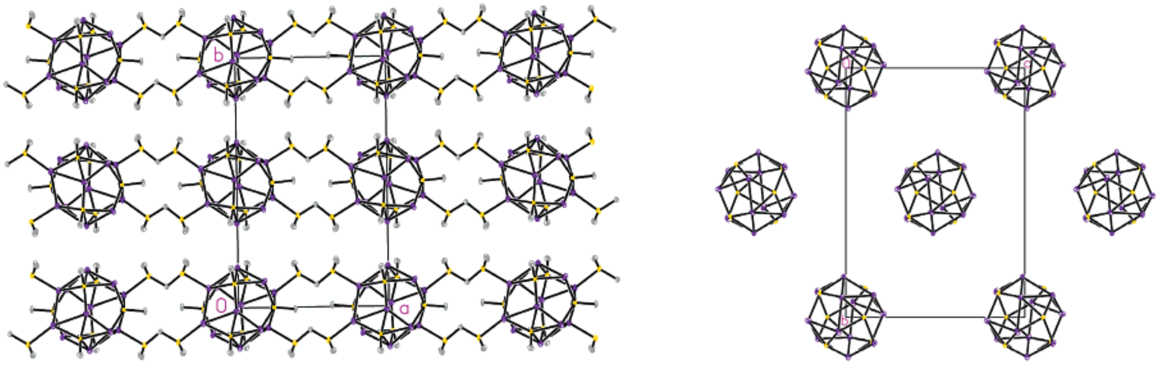


(a) (b)

Figure 1. (a) Asymmetric unit and atomic numbering of **1**. (H atoms and minor parts of the disordered fluorine atoms have been omitted for clarity.) (b) Atlas-sphere cluster of **1**. The μ_4-S bridges four silver atoms. (H atoms, trifluoroacetate groups, and bis(methylthio)methane have been omitted for clarity.)



(a) (b)

Figure 2. (a) Clusters in **1** are interconnected through the bis(methylthio)methane spacers, forming chains parallel to the *a* axis. (The trifluoroacetate groups and the H atoms have been omitted for clarity.) (b) Packing diagram of **1**, viewed down the chain axis (the *a* axis), showing the hexagonal packing of cylindrical rods.

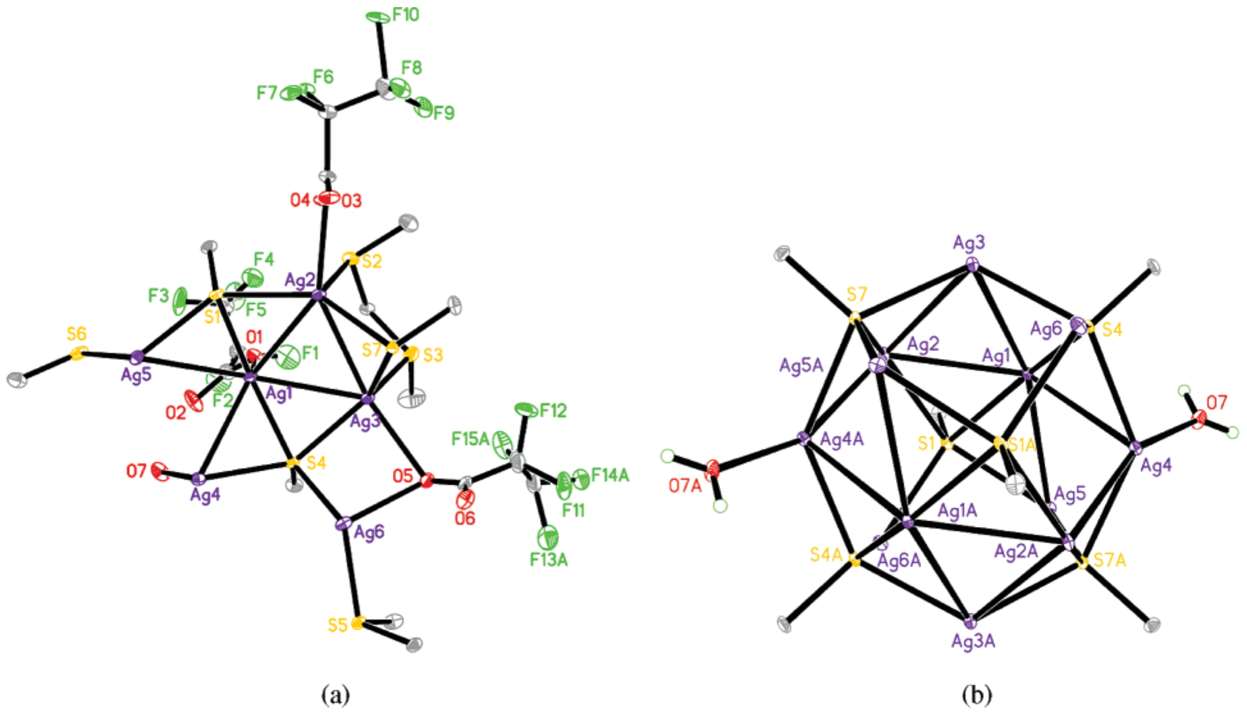
Scheme 1 [a]

(a) (b) (c)

[a] (a) Perfect cuboctahedron with square and equilateral triangular faces. (b) Distorted cuboctahedron made of the 12 Ag atoms in **1**. There is a Ag atom at each corner of the polyhedron. (c) $Ag_{12}S_6$ cluster in **1**. The black circles above each of the distorted square faces represent the sulfur atoms.

through its sulfur atoms, producing a five-membered ring, Ag(2)−S(1)−C(11)−S(2)−Ag(4) (Figure 1 and Scheme 2c).

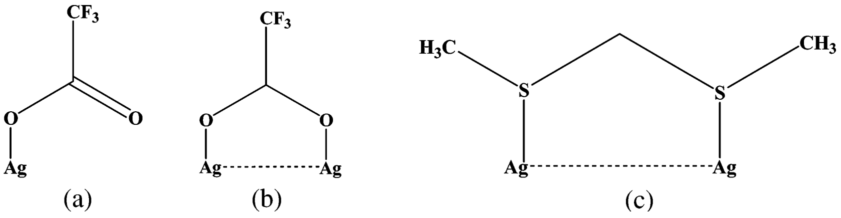
This kind of coordination was observed when L^{1-Me} was self-assembled with the methylsulfonate or the succinate silver(I) salts.[11] Second, four L^{1-Me} spacers link one $[Ag_{12}(CF_3CO_2)_6(L^{1-Me})_6(SCH_3)_6]$ cluster to two others to form a 1D coordination polymer parallel to the *a* axis (Figure 2a). The solid-state organization of this metal-organic



(a) (b)

Figure 3. Complex **2**. (a) Content of the asymmetric unit and atomic numbering. (b) Centrosymmetric cluster with the two water molecules coordinated to the Ag(4) atoms.

Scheme 2



(a) (b) (c)

coordination polymer may be best described as a hexagonal packing of cylindrical rods (Figure 2b).

In this complex, the silver atoms present different coordination modes, from 5 to 7. Atom Ag(6) has a coordination of 5, whereas Ag(1), Ag(4), and Ag(5) have a coordination of 6. The Ag(2) and Ag(3) atoms have a coordination of 7 (Figure S1). The silver−silver distances, which range from 2.9250(5) to 3.3615(6) Å, are shorter than the sum of the van der Waals radii, 3.44 Å,[33] and the shorter distance, 2.9250(5) Å, is slightly longer than 2.89 Å, which is twice the metallic radius of silver (Table S1).[33] According to the literature, there may be some weak interactions between the metal centers.[34−36]

$[Ag_6(CF_3CF_2CO_2)_3(L^{1-Me})_2(SCH_3)_3(H_2O)]_\infty$ (2). The X-ray analysis of **2** reveals the existence of a $Ag_{12}S_6$ cluster comparable to that of **1**. These two clusters are nearly identical except for the presence of two water molecules in **2**. The repeat unit of this complex consists of $[Ag_{12}(CF_3CF_2CO_2)_6(L^{1-Me})_4(SCH_3)_6(H_2O)_2]$ (Figure 3). In this complex, L^{1-Me}, $CF_3CF_2CO_2^-$, H_2O, and μ_4-SCH_3 groups are all bound to silver atoms. The silver−silver distances in **2**, which range from 2.961(1) to 3.380(1) Å, indicate, as they do for **1**, the presence of some weak argentophilicity (Table S1).[34−36]

The description of **2** follows that of **1**. The disordered pentafluoropropionate group displays a monodentate bridging mode and a dibridging mode in association with two metal centers. The bis(methylthio)methane ligand has two kinds of coordination modes. First, L^{1-Me} dibridges two silver(I) centers (Scheme 2c). Second, four L^{1-Me} organic connectors join one $[Ag_{12}(CF_3CF_2CO_2)_6(L^{1-Me})_4(SCH_3)_6(H_2O)_2]$ cluster to two others, thus developing into a 1D coordination polymer parallel to the *a* axis (Figure 3). The two water molecules are centrosymmetrically related. The O(7) water molecule (Ag(4)−O(7) = 2.385(7) Å) completes the coordination sphere of the Ag(4) atom. In turn, this water molecule is strongly hydrogen bonded to the oxygen atoms of two pentafluoropropionates. The first H bond between O(7) and the O(2) atom of a pentafluoropropionate is characterized by O(2)−O(7), 2.741(1) Å and O(7)−H···O(2), 167.3°.

The second H-bond interaction takes place between the water molecule of a cluster and the $CF_3CF_2CO_2^-$ group in

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(33) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*; Academic Press: San Diego, CA, 1994; pp 168, 180.
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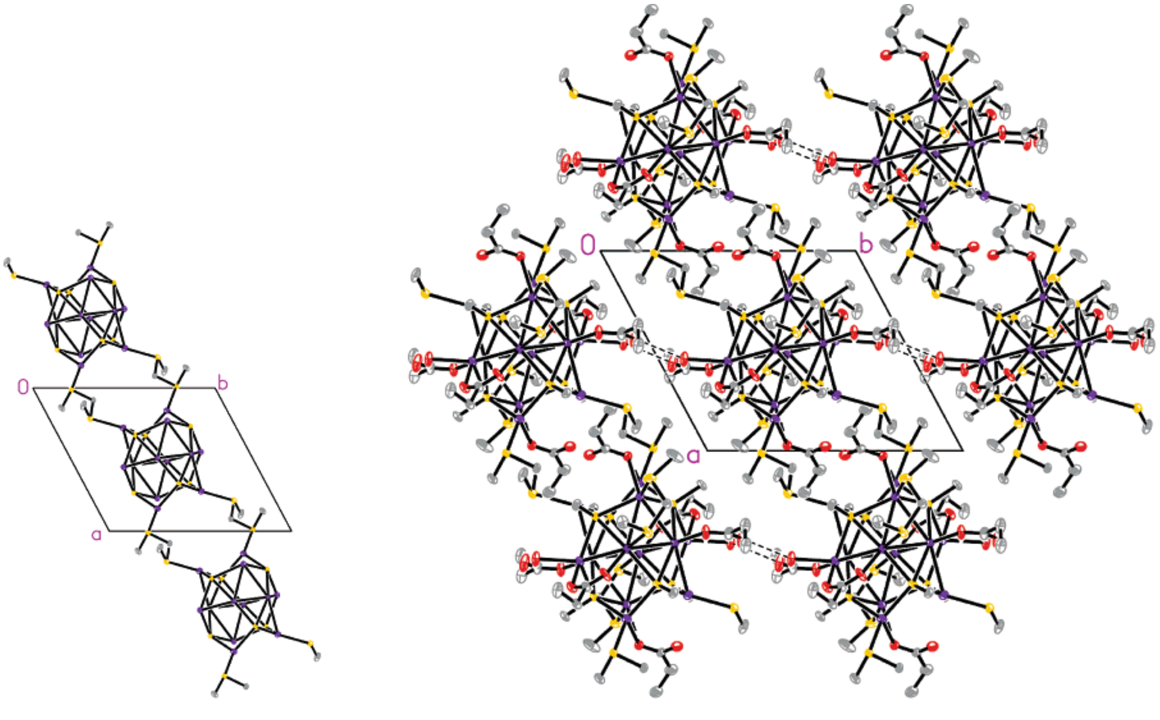

(a) (b)

Figure 4. Complex **2**. (a) One-dimensional association of clusters resulting in chains parallel to the *a* axis. (b) Disposition of the chains on the *ab* plane showing the H bonding and revealing the hexagonal environment of the clusters.

Table 2. Summary of the Structures Observed for Some Complexes of Silver(I) Salts and Bis(methylthio)methane

trifluoroacetate	pentafluoropropionate	heptafluorobutyrate
clusters in 1D coordination polymer $[Ag_6(CF_3CO_2)_3(L^{1-Me})_3(SCH_3)_3]$	$[Ag_6(CF_3CF_2CO_2)_3(L^{1-Me})_2(SCH_3)_3\ (H_2O)]$	not observed
2D coordination network $[AgL^{1-Me}(CF_3CO_2)]$	not observed	$[AgL^{1-Me}(CF_3CF_2CF_2CO_2)]$

an adjacent coordination polymer (O(7)−O(2)#2, 2.818(1) Å; O(7)−H···O(2), 160.9°; symmetry code for #2: $-x + 1, -y, -z + 2$) (Table S2). Thus, this second H bond linking polymeric chains gives rise to a 2D coordination polymer parallel to the (001) plane (Figure 4b).

The Ag−S distances for the μ_4-SCH_3 unit range from 2.443(2) to 2.553(3) Å, which are in the normal interval for $Ag_4(\mu_4\text{-}SR)$ (2.577(5)−2.690(5) Å).[29,30,32] The Ag−S separation (2.429(2)−2.691(3) Å) when the bis(methylthio)methane is coordinated to the Ag(I) ions compares well to those in the silver dithioether coordination polymers (2.434(2)−2.697(1) Å) (Table S3).[11,31] We note that there exist Cu(I) complexes whose structures are related to ours. The crystal structures of two Cu(I) complexes containing the $Cu_{12}S_6$ cluster and quadruply bridging zwitterionic thiolate ligands were reported by Prichard et al.[37]

The similarities stop here because the $Cu_{12}S_6$ clusters, bridged to one another through Br or Cl atoms coordinated to Cu(I) atoms, form a 2D network.

Supramolecular Isomerism and Topology. We have just described two 1D coordination polymers, **1** and **2**, which are topologically identical. Interestingly, the reaction of bis(methylthio)methane and silver trifluoroacetate, which yields **1**, also produces the 2D coordination network $[AgL^{1-Me}(CF_3CO_2)]_\infty$ much more easily. This latter complex is, in turn, topologically related to the heptafluorocarboxylate, $[AgL^{1-Me}(CF_3CF_2CF_2CO_2)]_\infty$ (Figure S3).

The relationship between the four silver(I) complexes of bis(methylthio)methane and the three perfluorocarboxylate anions is summarized in Table 2. It was the attempt to synthesize the analogous pentafluoropropionate that led to the discovery of **1** and **2**. Attempts to synthesize the related heptafluorobutyrate incorporating the $Ag_{12}S_6$ cluster were unsuccessful.

Comment on μ_4-SCH$_3$. The μ_4-SCH_3 entities bridging four adjacent silver(I) centers were observed in **1** and **2**. Each of these species comes from the C−S cleavage of the $CH_3SCH_2SCH_3$ organic building block, L^{1-Me}. In addition, the GC/MS of L^{1-Me} shows a mean peak at 108 that corresponds to the L^{1-Me} and another one at 61 that matches the $CH_3SCH_2^+$ entity. C−S cleavage of dithiolates is not uncommon. For example, Jeannin et al. described the structure of the $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SC_2H_5)_2]$ cluster obtained by the self-assembly process of $[Fe_3(CO)_{12}]$ and $CH_3{-}C{\equiv}C{-}SC_2H_5$.[30] The unsymmetrical $CH_3{-}C{\equiv}C{-}SC_2H_5$ building block undergoes a C−S cleavage during the synthesis of that complex.

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(37) Prichard, R. G.; Parish, R. V.; Salehi, Z. *J. Chem. Soc., Dalton Trans.* **1999**, 243.

Prichard et al. indicated that zwitterionic ligands were a requisite for their $Cu_{12}S_6$ cluster to form.[37] However, this is not a requirement for the syntheses of $Ag_{12}S_6$ clusters. That a cleavage is noted in two L^{1-Me} complexes is surprising because there are many structures containing the dithioether family of ligands, L^{n-R}, but none involving the presence of a cluster. It could be that the small size of the ligand ($n = 1$ and R = Me) is the controlling factor. However, because **1** has a polymorph that does not contain a cluster, it is not clear how the same L^{1-Me} ligand is at times the subject of C−S cleavage whereas at other times it retains its structure.

Conclusions

Unusual 1D coordination polymers are observed in complexes of bis(methylthio)methane with silver(I) trifluoroacetate or silver(I) pentafluoropropionate. In both complexes, a $Ag_{12}S_6$ cluster is formed with a fragment of the ligands and the silver(I) centers. The clusters incorporate the $^{-}SCH_3$ anion, in μ_4-SCH_3 coordination, which is obtained through the breakup of some of the ligand molecules. The clusters are associated through the bis(methylthio)methane ligands in a double-chain 1D coordination polymer. The pentafluoropropionate complex incorporates silver-coordinated water molecules. These form hydrogen bonds that connect adjacent chains in a 2D coordination network.

We note that no cluster could be obtained with the longer heptafluorobutyrate. Although numerous complexes containing the L^{n-R} ligand ($n = 1-10$ and R = Me, Et, Ph, tBu, Benz) have been reported, it is only with the smallest one, L^{1-Me}, that clusters can be formed, albeit with difficulty.

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Supporting Information Available: X-ray crystallographic information files for **1** and **2**, structures of coordination polyhedra around the silver atoms in **1** and **2**, and the structure of the polymorph of the trifluoroacetate and the related heptafluorobutyrate. Silver−silver distances, characteristics of the hydrogen bonds, and selected bond distances and angles in **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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