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Mesitylgold(I) and Silver(I) Perfluorocarboxylates as Precursors of Supramolecular Au/Ag Systems

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Reaction of $[Ag(CF_3CO_2)]$ with tetrahydrothiophene (tht) (2:1) in dichloromethane leads to the synthesis of $[Ag_4(CF_3CO_2)_4(tht)_2]$ (**1**), which further reacts with mesitylgold(I) ([Au(mes)]) (1:1) to afford $[AuAg_4(mes)(CF_3CO_2)_4(tht)]_n$ (**3**). Treatment of [Au(mes)] with $[Ag(RCO_2)]$ (R = CF_3, CF_2CF_3) and tht (molar ratio 1:4:1 or 1:4:3) leads to the new Au/Ag systems $[AuAg_4(mes)(RCO_2)_4(tht)_x]_n$ ($x = 1$, R = CF_3 (**3**), CF_2CF_3 (**4**); $x = 3$, R = CF_3 (**5**), CF_2CF_3 (**6**)). The crystal structures of **3**, **4**, and **6** have been established by X-ray diffraction, all of them displaying Au···Ag interactions supported by mesityl ligands that bridge three metal centers in an unprecedented situation in transition metal chemistry. Additional Au−S−Ag and Ag−O−Ag (**3** and **4**) or Ag−S−Ag (**6**) bonds result in two-dimensional polymers that contain both Au···Ag and Ag···Ag contacts. Treatment of **3** with water (1:2) in dichloromethane leads to $\{[AuAg_4(mes)(CF_3CO_2)_4(tht)(H_2O)]\cdot H_2O\cdot CH_2Cl_2\}_n$ (**7**), whose crystal structure shows the partial break of the cyclic $[Ag_2(\mu\text{-}RCO_2)_2]$ dimer present in the structures of **3**, **4**, and **6**, probably caused by the coordination of one molecule of water to one of the Ag^I centers. It also displays Au···Ag and Ag···Ag interactions, as well as Ag−C bonding interactions and additional Ag−O contacts, which result in a monodimensional polymer. The crystal structure of **1** has also been determined by X-ray diffraction.

Introduction

Although aurophilic Au(I)···Au(I) interactions are the most studied among nonbonding contacts between closed-shell metals,[1] a number of species displaying Au(I)···Ag(I) interactions have been recently described. Most of them are complexes that contain bidentate ligands between Au^I and Ag^I,[2] but there are also compounds in which such interactions are supported only by aryl bridging ligands[3] or even a number of examples that display unsupported Au···Ag interactions.[4] Among the latter, additional intermolecular Au···Au contacts can also be found, as in $[Au_2Ag_2(C_6F_5)_4L_2]$ (L = SC_4H_8, C_6H_6)[4a,b] or in $\{Ag([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2\}BF_4$ (bzim = 1-benzylimidazolate),[4c,d] resulting in the formation of monodimensional polymers in the solid state.

On the other hand, donor-free silver(I) perfluorocarboxylates have been shown to often crystallize forming cyclic dimers of the type $[Ag(\mu\text{-}O,O'\text{-}RCO_2)]_2$ with planar eight-membered rings that display intramolecular Ag···Ag interactions.[5] This dimeric unit can also be kept as a core in complexes with neutral donor ligands, either preserving[2a,6] or losing[7] the metallophilic contacts, or even in Au^I/Ag^I compounds, such as in the tetranuclear $[\{(4\text{-}Me_2NC_6H_4)Ph_2PAu(OCOC_2F_5)\}_2(AgC_2F_5CO_2)_2]$[2a] or $[\{(C_6F_5)Au(PPh_2CH_2SPh)\}_2(AgCF_3CO_2)_2]$,[2b] which displays both Au···Ag and Ag···Ag interactions. By contrast, in the pyramidal complex $[NBu_4]_2[AuAg_4(3,5\text{-}C_6F_3Cl_2)_2(CF_3CO_2)_5]$

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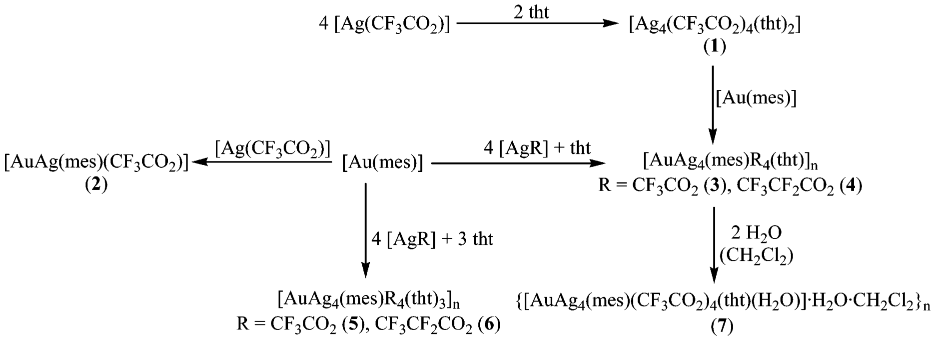
Scheme 1. Synthesis of Complexes 1−7



prepared by reaction of NBu$_4$[Au(3,5-C$_6$F$_3$Cl$_2$)$_2$] with [Ag(CF$_3$CO$_2$)] and NBu$_4$(CF$_3$CO$_2$) (1:4:1),[3e] also containing Au···Ag and Ag···Ag contacts, the silver atoms and the trifluoroacetate anions present a different disposition giving rise to a 19-membered bicycle with the silver centers forming the base of a square pyramid (the gold(I) atom occupies the apical position). Even in the absence of a heterometal, a change in the dimeric structure of the [Ag(RCO$_2$)]$_2$ unit can occur during the reaction with a neutral substrate, as observed in the recently described complex [(Ph$_3$PS)$_4$(AgO$_2$CCF$_3$)$_6$],[6f] which displays a 24-membered metallacycle containing six silver(I) centers and six carboxylate OCO units.

Considering all these precedents, we wondered if we could obtain heterometallic Au^I/Ag^I systems with Au···Ag interactions by reaction of a gold(I) substrate with silver perfluorocarboxylates. The pentameric [Au(mes)]$_5$ (mes = 2,4,6-C$_6$H$_2$Me$_3$) was selected as gold starting material considering that the mesityl groups could facilitate the presence of Au···Ag contacts, due to the capability of mesityl to act as bridging ligand, and that it could lead to a novel and interesting structural situation.

We were also interested in the study of the factors that can influence the retention of the cyclic dinuclear core [Ag(μ-O,O′-RCO$_2$)]$_2$ in the resulting complexes, and for this reason, we carried out the reaction of [Au(mes)]$_5$ with [Ag(RCO$_2$)] (R = CF$_3$, CF$_2$CF$_3$) in the presence or absence of a neutral donor ligand, such as tetrahydrothiophene (tht) or water, and in different solvents and molar ratios. We also studied the reaction of [Ag(CF$_3$CO$_2$)] with tht in different molar ratios in order to determine if the eight-membered ring is maintained.

Results and Discussion

Reaction of [Ag(CF$_3$CO$_2$)] with tht (2:1) in dichloromethane leads to the synthesis of [Ag$_4$(CF$_3$CO$_2$)$_4$(tht)$_2$] (**1**) as a white solid, whose analytical and spectroscopic data agree with the incorporation of half a molecule of tetrahydrothiophene per silver atom (see Scheme 1). Thus, its IR spectrum shows, among others, absorptions at 1663 (vs, br) and 1209 (vs, br) cm^{-1} due to the trifluoroacetate anions and at 1263 (vs) cm^{-1} characteristic of the tht molecules. The ^{19}F and ^{1}H NMR spectra of **1** corroborate the presence of both anionic and neutral ligands, respectively, the former displaying a singlet at −73.5 ppm and the latter two multiplets at 3.13 and 2.07 ppm.

Finally, by slow diffusion of hexane into a solution of **1** in dichloromethane single crystals of **1** adequate for X-ray diffraction studies were obtained, which show that the dimeric unit present in many other related complexes[2a,6,7] is opened now into a higher nuclearity one. The crystal structure of **1** is shown in Figures 1 and 2, in which a 18-membered bicycle can be observed with the four silver atoms in a butterfly disposition bridged by the trifluoroacetate anions and the sulfur atom of

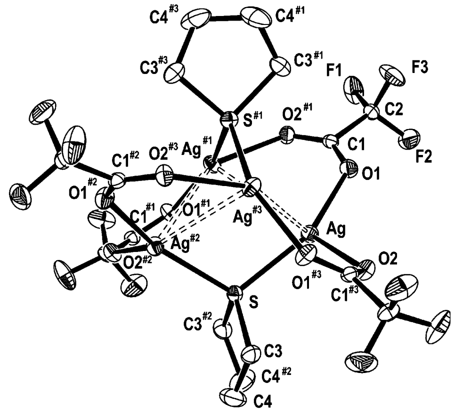


Figure 1. Molecular structure of complex **1** with the labeling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.

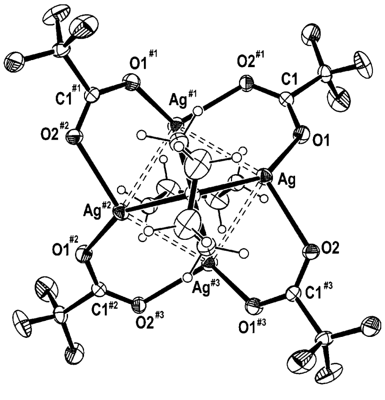


Figure 2. Molecular structure of complex **1** viewed down the 4-fold screw axis. Hydrogen atom have been omitted for clarity.

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the neutral tht ligands. Complex **1** crystallizes in the $I4_1/a$ space group of the tetragonal system with four molecules in the unit cell and only a quarter of a molecule residing in the asymmetric unit. The neighboring silver centers maintain Ag···Ag contacts of 3.2856 (5) Å, longer than those found in most of the structures of complexes of the type $[Ag_2(RCO_2)_2L_n]$ ($n = 1, 2$) that display such contacts (from 2.8669(9) to 3.3813(6) Å).[6] The trifluoroacetate anions are asymmetrically bridging two silver atoms, showing Ag−O bond distances of 2.921(3) and 2.416(3) Å, similar to what is observed in $[Ag_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-dcpm})]$ (dcpm = bis(dicyclohexylphsophino)methane),[6b] which displays a short (2.191(3) Å) and a long (2.446(4) Å) Ag−O bond distance. Finally, the Ag−S bond distance of 2.4421(8) Å compares well with those found in $[Au_2Ag_2(C_6F_5)_4(SC_4H_8)_2]_n$[4a,b] (2.454(4) Å) and $[NBu_4][\{Pt(C_6F_5)_2\}_2(\mu\text{-}C_6F_5)_2\{\mu\text{-}Ag(SC_4H_8)\}]\cdot 0.5C_6H_{14}$[8] (2.421(3) Å), which contain terminal tht molecules, and is shorter than the Ag−S distances observed in $[Ag(O_3SCF_3)(SC_4H_8)]_n$[9] (2.4897(9) and 2.4963(9) Å), $[\{(Ph_3P)Au(\mu\text{-mes})Ag(SC_4H_8)\}_2][SO_3CF_3]_2$[3a] (2.8245(6) Å), and $[NBu_4][Pt_2Ag(C_6F_5)_6(\mu\text{-}SC_4H_8)_2]$[10] (2.778(2) and 2.547 Å), in which the tht's act as bridging ligands, as in complex **1**.

We tried then to synthesize other compounds with different proportions of tht, but when the same reaction is carried out in different molar ratios or compound **1** is treated with an excess of tht, the same complex (**1**) is isolated or no reaction is observed, respectively.

On the other hand, when $[Ag(CF_3CO_2)]$ is treated with equimolecular amounts of mesitylgold(I) in dichloromethane and in the absence of tht, the new complex $[AuAg(mes)(CF_3CO_2)]$ (**2**) is isolated from the solution as a dark green powder. The same solid is always formed when the reaction is carried out in different molar ratios of the reagents, when donor solvents, such as acetone or tetrahydrofuran, are employed, or when the solvent is not distilled and dehydrated. Its analytical and spectroscopic data agree with the proposed formulation, and thus, its IR spectrum shows absorptions arising from the mesityl group at 1592 (s) and 851 (s) cm^{-1} and from the trifluoroacetate at 1658 (vs, br) and 1186 (vs, br) cm^{-1}. The former appear at wavelengths nearly identical to those corresponding to the starting complex $[Au(\mu\text{-mes})]_5$, while the latter are similar to those described above for complex **1** and suggest the presence of coordinated trifluoroacetate anions. The presence of the mesityl group is also confirmed in its ^{1}H NMR spectrum, which displays two singlets located at 2.17 and 2.84 ppm for the hydrogen atoms of the methyl substituents in *para* and *ortho* positions and a third singlet at 6.89 ppm, due to the protons located in the *meta* positions. These positions, similar to those of the starting complex $[Au(\mu\text{-mes})]_5$ (2.15, 2.63, and 6.76 ppm), suggest the presence of the mesityl group acting as a bridging ligand and a similar structural disposition for the gold atoms and mesityl groups in solution in both cases. Regarding its ^{19}F NMR, it is very similar to that of compound **1**, showing a singlet at −73.2 ppm, which seems to indicate a similar behavior of the anions in both complexes. Although our efforts to obtain single crystals of **2** to determine its structure in the solid state were unsuccessful, its mass spectrum (ES-) suggests an, at least, oligomeric nature for this complex, displaying, among others, a peak at $m/z = 870$, which corresponds to the unit $[Ag_2Au(mes)(CF_3CO_2)_3]^-$.

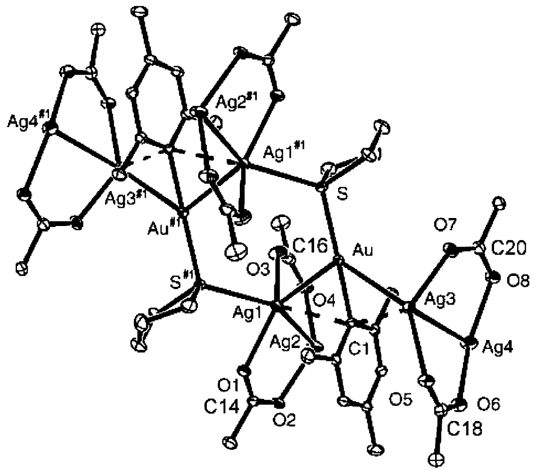

Figure 3. Part of the polymeric structure of complex **3** with the labeling scheme of the atom positions. Hydrogen and fluorine atoms have been omitted for clarity.

By contrast, a different result is obtained when there is a neutral ligand, such as tht, present in the reaction medium. Thus, when mesitylgold(I) is treated with $[Ag_4(CF_3CO_2)_4(tht)_2]$ (**1**) (1:1) in dichloromethane, a new compound of stoichiometry $[AuAg_4(mes)(CF_3CO_2)_4(tht)]_n$ (**3**) is isolated as a pale yellow solid. This implies the loss of one molecule of tetrahydrothiophene from the starting product **1**. In accordance with this, the same product **3** can be prepared in one step by reaction of [Au(mes)] with $[Ag(CF_3CO_2)]$ and tht (1:4:1) (Scheme 1). The FT-IR spectrum of compound **3** shows absorptions arising from the three types of ligands: tetrahydrothiophene, mesityl, and trifluoroacetate. Its ^{1}H NMR spectrum confirms the presence of both tht and mesityl ligands in a 1:1 molar ratio, showing two multiplets at 3.13 and 2.07 ppm for the methylenic hydrogen atoms of the tetrahydrothiophene and three singlets at 2.30, 2.47, and 6.98 ppm for the protons of the mesityl group. The latter are significantly shifted compared with those described for complex **2** and mesitylgold(I), where they appear at 2.17, 2.84, and 6.98 ppm (**2**) and at 2.15, 2.63, and 6.76 ppm ([Au(mes)]). This could be due to the coordination of a molecule of tht *trans* to the mesityl group in **3**, which is neither present in complex **2** nor in mesitylgold(I), or to a different structural arrangement for the mesityl groups and gold centers in both cases. Regarding the ^{19}F NMR spectrum of **3**, it shows a unique singlet, which suggests the equivalence of all the trifluoroacetate anions in solution. As in the case of complex **2**, its mass spectrum (ES-) suggests an oligomeric or polymeric nature for **3**, displaying peaks at m/z 775 and 870, corresponding to the fragments $[Ag_3(CF_3CO_2)_4]^-$ and $[AuAg_2(mes)(CF_3CO_2)_3]^-$, respectively.

Finally, the crystal structure of **3** was determined by X-ray diffraction methods from single crystals obtained by slow diffusion of hexane into a solution of **3** in dichloromethane. It can be described as decanuclear $[AuAg_4(mes)(CF_3CO_2)_4(tht)]_2$ units formed by two [Au(mes)(tht)] and four $[Ag_2(CF_3CO_2)_2]$ fragments linked via Au−Ag, Ag−S, and Ag−C bonding interactions, as shown in Figure 3. The repetition of such decanuclear units joined together through additional Ag−O contacts of 2.429(3), 2.518(3), and 2.516(3) Å gives rise to a two-dimensional polymer (Figure 4). As is foreseeable, these Ag−O distances are longer than those found within the $[Ag_2(CF_3CO_2)_2]$ units, which range from 2.151(3) to 2.367(3) Å. Both the dimers and the intramolecular Ag···Ag interactions are kept in the crystal structure of **3**, showing Ag−Ag distances (2.9149(5) and 2.9754(5) Å) that compare well with those found in complexes of the type $[Ag_2(RCO_2)_2L_n]$ ($n = 1, 2$) that display

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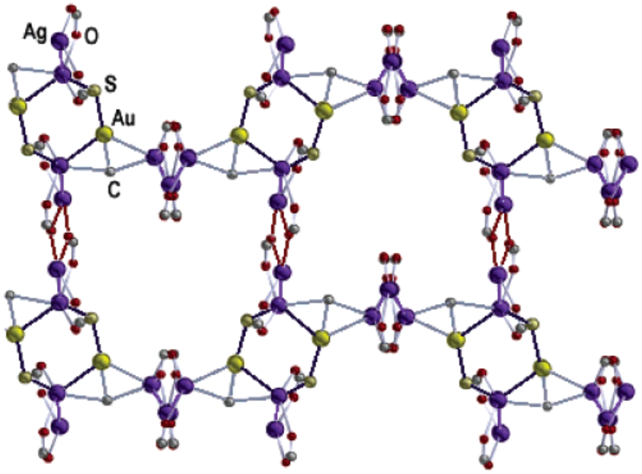


Figure 4. Polymeric layer structure of complex **3**. Hydrogen and fluorine atoms, as well as the carbon atoms of the tht and mes ligands (except the *ipso* carbon), have been omitted for clarity reasons. Hexanuclear $Ag_2Au_2S_2$ rings are marked in black and Ag−O−Ag bridges in red.

such contacts (2.8669(9)−3.3813(6) Å).[6] Each gold center is linearly coordinated to the *ipso* carbon atom of a mesityl group and to the sulfur of a tht ligand with typical Au−C and Au−S bond distances of 2.045(4) and 2.3195(11) Å, respectively, and maintain short Au···Ag contacts of different magnitude (2.8226(4) and 2.8993(4) Å) with two neighboring silver centers. The former is nearly identical to the Au−Ag distance of 2.8245(6) Å found in the related mesityl derivative $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2][SO_3CF_3]_2$,[3a] in which both metals are also bridged by a mesityl ligand, or in the dinuclear complex $[AuAg(PPh_2py)_2(OClO_3)_2]$[2d] (2.820(1) Å), where the metal centers are doubly bridged by diphenylphosphinopyridine. The Au···Ag interactions in **3** are in general weaker than in most of the complexes containing aryl bridging ligands between gold and silver (2.7758(8)−2.8245(6) Å),[3a−d] with the only exception of $(NBu_4)_2[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(CF_3CO_2)_5]$,[3e] where the Au−Ag distances range from 2.9010(6) to 3.0134(6) Å.

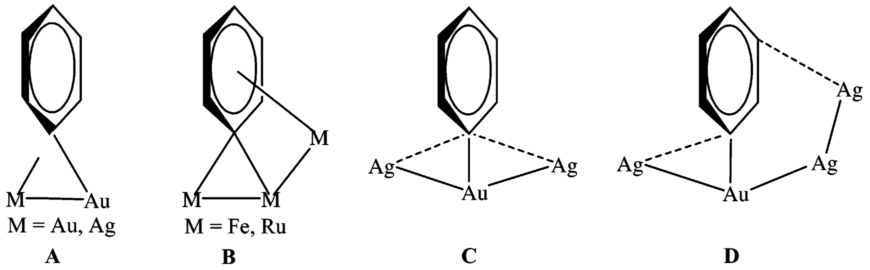
It is worth noting that although there are some examples of compounds with aryl groups acting as bridges between two metal atoms though the *ipso* carbon of the aryl ligand[3] (see Chart 1, **A**) or even as a bridge between three group-8 metal centers as shown in Chart 1, **B**,[11] interestingly, the *ipso* carbon atom of the mesityl ligand in **3** bridge three metals (see Chart 1, **C**), which is an unprecedented situation in transition metal chemistry. Thus, the *ipso* carbon atom binds the gold center and two silver atoms, showing longer Ag−C distances (2.614(4) and 2.530(4) Å) than those observed in the rest of complexes containing aryl bridging ligands between Au^I and Ag^I (in the range 2.27(2)−2.506(8) Å),[3] in which the *ipso* carbon atom binds two instead of three metals. In contrast, the Au−C distance of 2.045(4) Å observed in **3** is oddly shorter than those found in the same related complexes (2.067(7)−2.200(7) Å).[3]

Apart from the mesityl, the sulfur atom of the tht also acts as a bridge between a Au(I) center and a Ag(I) atom, thus forming, together with one of the Au···Ag contacts, hexanuclear $Ag_2Au_2S_2$ rings (see Figure 3). It is worth mentioning that, although there are a number of compounds with tetrahydrothiophene bridging two metals, complex **3** is the first case in which this ligand acts as a bridge between gold and any other metal, and there are a few structures with tht bonded to gold and none of them contain an aryl or alkyl group as ligand.[12] The Au−S distance in **3** (2.3195(11) Å) is similar to those observed in complexes with tht *trans* to a neutral ligand, such as $\{[Au(tht)_2][AuI_2]\}_n$[12a] (2.335(6) and 2.30(7) Å), $[Au(tht)_2](o\text{-}C_6H_4(SO_2)_2N)$[12b] (2.295 Å), or $[Au(tht)(PPh_2py)]ClO_4$[12c] (2.321(2) Å), but longer than the Au−S bond lengths found in those that have an anionic ligand *trans* to tht, such as $[Au\{N(SO_2R)_2\}(tht)]$ (R = CH_3, $p\text{-}C_6H_4Cl$, $p\text{-}C_6H_4I$)[12d] (2.237−2.263 Å) or [AuX(tht)] (X = Cl, Br)[12e] (2.279 and 2.256 Å). The Ag−S distance of 2.6877(11) Å shows a weaker bond than in complex **1** (2.4421(8) Å) or in $[Ag(O_3SCF_3)(SC_4H_8)]_n$[9] (2.4897(9) and 2.4963(9) Å), but is shorter than that described for the related complex $[\{(Ph_3P)Au(\mu\text{-mes})Ag(SC_4H_8)\}_2][SO_3CF_3]_2$[3a] (2.8245(6) Å), in which the tht acts as a bridge between two silver(I) atoms, or in $[NBu_4][Pt_2Ag(C_6F_5)_6(\mu\text{-}SC_4H_8)_2]$[10] (2.778(2) and 2.547 Å).

Similarly, treatment of [Au(mes)] with $[Ag(CF_3CF_2CO_2)]$ and tht (1:4:1) affords a complex of stoichiometry $[AuAg_4(mes)(CF_3CF_2CO_2)_4(tht)]_n$ (**4**) (Scheme 1). Its FT-IR spectrum resembles that of complex **3**, and also its ^1H NMR spectrum is very similar to that mentioned above for **3** and confirms the presence of tht and mesityl in equimolecular amounts displaying two multiplets at 3.16 and 2.10 ppm for the hydrogen atoms of tht and three singlets at 2.32, 2.46, and 7.00 ppm for the protons of the mesityl group. The perfluoropropionate anions are also detected as equivalent in solution in the ^{19}F NMR spectrum of **4**, which displays two singlets at −83.2 and −118.8 ppm. A certain degree of association is also suggested, as in previous cases, in its mass spectrum (ES-), which displays peaks at *m*/*z* 433, 704, and 977, corresponding to the fragments $[Ag(CF_3CF_2CO_2)_2]^-$, $[Ag_2(CF_3CF_2CO_2)_3]^-$, and $[Ag_3(CF_3CF_2CO_2)_4]^-$, respectively.

Finally, its crystal structure was established by X-ray diffraction from single crystals obtained by slow diffusion of hexane into a solution of **4** in dichloromethane. It is shown in Figures 5 and 6, which show a crystal structure similar to that described above for compound **3** consisting of decanuclear $[AuAg_4(mes)(CF_3CF_2CO_2)_4(tht)]_2$ units linked together through Ag−O contacts, resulting in a two-dimensional polymer normal to the crystallographic *y* axis (Figure 6). As in the case of complex **3**, these Ag−O interactions, of 2.408(6), 2.417(6), and 2.532(6) Å, are longer than those found within the $[Ag_2(CF_3CF_2CO_2)_2]$ units (from 2.196(7) to 2.367(6) Å). The silver centers in these dimers still maintain the Ag···Ag interactions, showing distances of 2.9479(10) and 2.9295(10) Å, similar to those found in **3** or in other complexes containing the dimeric

Chart 1. Different Coordination Modes of Aryl Bridging Ligands



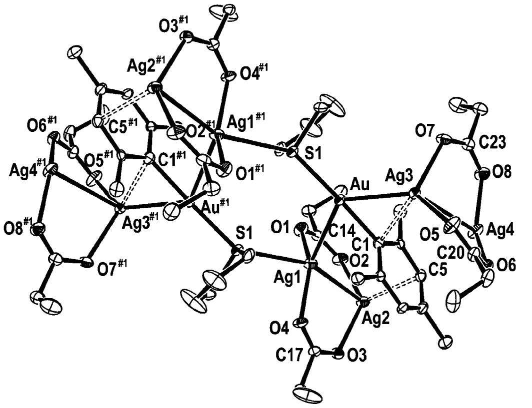


Figure 5. Part of the polymeric structure of complex **4** with the labeling scheme of the atom positions. Hydrogen and fluorine atoms have been omitted for clarity.

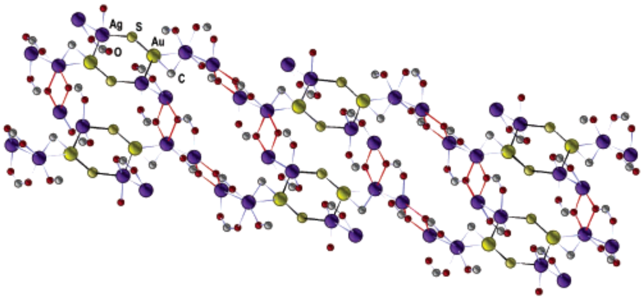


Figure 6. Polymeric layer structure of complex **4**. Hydrogen and fluorine atoms, as well as the carbon atoms of the tht and mes ligands (except the *ipso* carbon), have been omitted for clarity reasons. Hexanuclear $Ag_2Au_2S_2$ rings are marked in black and Ag−O−Ag bridges in red.

unit $[Ag_2(RCO_2)_2]$.[6] There are also intermetallic Au···Ag short contacts of 2.8140(8) and 2.8166(8) Å connecting the $[Ag_2(CF_3CF_2CO_2)_2]$ fragments with the [Au(mes)(tht)] units, which, as in **3**, are in general longer than in most aryl-bridged complexes (2.7758(8)−2.8245(6) Å).[3a−d] Surprisingly, the Au−Ag lengths in **4** are nearly identical, although only one of the silver atoms binds the *ipso* carbon atom of the mesityl ligand, and are shorter than in complex **3**, where two different Au−Ag distances are observed (2.8226(4) and 2.8993(4) Å), although they should be more symmetric considering the bonding scheme in **3** (see Figure 3). As in the structure of **3**, each gold(I) center displays its typical linear coordination and bridging tht ligands responsible of the presence of $Ag_2Au_2S_2$ rings (see Figure 5). The Au−C distance of 2.047(8) Å is almost identical to that in complex **3** (2.045(4) Å), although the carbon atom in **4** bridges two instead of three metal centers, and is also shorter than the Au−C bond lengths found in related complexes (2.067(7)−2.200(7) Å).[3] Regarding the Au−S distance of 2.347(2) Å, as expected for a bridging tht, it is longer than in the complexes with gold(I) bonded to a terminal tht (2.237−2.335(6) Å)[12] and also longer than in **3** (2.3195(11) Å). The Ag−S distance of 2.888(2) Å is in this case also longer than in complexes **1** (2.4421(8) Å) and **3** (2.6877(11) Å) or in other compounds with bridging tht.[3a,9,10]

The main difference between the crystal structures of **3** and **4** is located in the bonding scheme of the mesityl ligand, which, as in **3**, very interestingly bridges one gold(I) and two silver(I) centers, although in a different and striking way (Chart 1, **D**): the *ipso* carbon atom binds the gold center and a silver atom (which also keep a short Au···Ag contact) with a Ag−C of 2.532(8) Å, while the second silver(I) center is connected to one of the *meta* carbon atoms of the mesityl group (Ag−C 2.650(8) Å), as shown in Figure 5. Both Ag−C distances are of the same order as those described above for complex **3** and also longer than in other complexes with aryl bridging ligands between Au and Ag (type **A**)[3] (Ag−C distances ranging from 2.27(2) to 2.506(8) Å).

In view of the interesting crystal structures found for complexes **3** and **4**, both containing tht, perfluorocarboxylate and mesityl bridges, as well as Au···Ag and Ag···Ag interactions, we wondered if the presence of a higher amount of tetrahydrothiophene would give rise to different dispositions, although, as commented above, treatment of $[Ag_4(CF_3CO_2)_4(tht)_2]$ (**1**) with mesitylgold(I) (1:1) takes place with the loss of one molecule of tht, resulting in the formation of **3**. In accordance with this, the reaction of [Au(mes)] with $[Ag(RCO_2)]$ (R = CF_3, CF_2CF_3) and tht (1:4:2) affords a mixture of $[AuAg_4(mes)(RCO_2)_4(tht)]_n$ (R = CF_3 (**3**), CF_2CF_3 (**4**)) and another product with a higher content of tht. In contrast, when the same reaction is carried out with 3 mol of tht per gold(I), the new products $[AuAg_4(mes)(RCO_2)_4(tht)_3]_n$ (R = CF_3 (**5**), CF_2CF_3 (**6**)) are isolated as pale yellow solids with analytical and spectroscopic data in accordance with the proposed stoichiometry (Scheme 1). Thus, their FT-IR spectra resemble those of complexes **3** and **4** (see Experimental Section), and their ^1H NMR spectra are very similar to those described for **3** and **4**, with relative intensities for the resonances due to tht and mesityl, which corroborate the presence of three molecules of tht (which are equivalent in solution) per mes ligand, as the main difference. The perfluorocarboxylate anions are detected, also as equivalent in solution, in their ^{19}F NMR, which show one (**5**) or two (**6**) singlets at −73.6 ppm or at −83.2 and −118.9 ppm, respectively. Finally, their mass spectra (ES-) display peaks at *m*/*z* 333 and 554 (**5**) or at *m*/*z* 433 and 704 (**6**), which correspond to the fragments $[Ag(RCO_2)_2]^-$ and $[Ag_2(RCO_2)_3]^-$, respectively.

By slow diffusion of hexane into a solution of **6** single crystals suitable for X-ray diffraction studies were obtained, and its crystal structure was determined (Figures 7 and 8). The asymmetric unit contains a $[Ag_2(CF_3CF_2CO_2)_2]$ dimer, a [Au(mes)(tht)] unit, and a $[Ag_2(CF_3CF_2CO_2)_2(tht)_2]$ fragment, which are connected via Au···Ag and Ag···C short contacts, as shown in Figure 7. The first difference between the crystal structures of **3** or **4** and **6** is the presence of three instead of two Au···Ag contacts of 2.8540(6), 2.8845(6), and 3.0782(6) Å, distances that compare well with the Au···Ag lengths in **3** (2.8226(4) and 2.8993(4) Å), but are longer than in **4** (2.8140(8) and 2.8166(8) Å) and in most of the related complexes containing aryl bridging ligands between gold and silver (2.7758(8)−2.8245(6) Å),[3a−d] with the exception of $(NBu_4)_2[Au(3,5\text{-}C_6F_3Cl_2)_2Ag_4(CF_3CO_2)_5]$,[3e] which presents the longest Au−Ag distances described to date (2.9010(6)−3.0134(6) Å). Another

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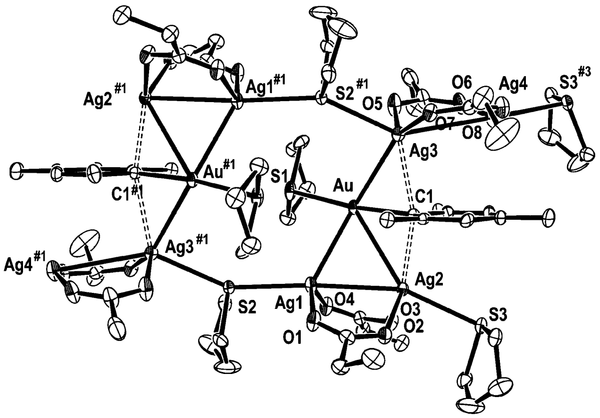

Figure 7. Part of the polymeric structure of complex **6** with the labeling scheme of the atom positions. Hydrogen and fluorine atoms have been omitted for clarity.

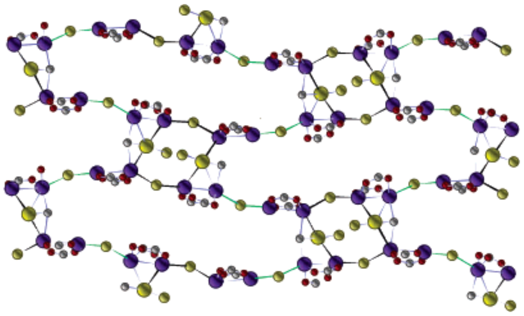

Figure 8. Polymeric layer structure of complex **6**. Hydrogen and fluorine atoms, as well as the carbon atoms of the tht and mes ligands (except the *ipso* carbon), have been omitted for clarity reasons. Octanuclear $Ag_4Au_2S_2$ rings are marked in black and Ag−S−Ag bridges in green.

difference is the presence of two additional tetrahydrothiophene molecules in one of the silver(I) trifluoroacetate dimers bonded to the Ag(I) centers with Ag−S bond distances of 2.6295(16) and 2.7116(17) Å. These additional tht molecules seem to be responsible for the different mode of polymerization of complex **6** compared with compounds **3** and **4**: the formation of Ag−S−Ag instead of Au−S−Ag bridges, which result in the appearance of eight-membered $Au_2Ag_4S_2$ rings, as shown in Figure 7, and finally in a two-dimensional polymer (Figure 8). Thus, the tht molecules bonded to silver asymmetrically bridge two Ag(I) centers, showing Ag−S bond lengths of 2.6295(16) and 2.7226(16) Å for S(2) and of 2.6574(17) and 2.7116(17) Å for S(3). As in the previous complexes **3** and **4**, both the dimers and the intramolecular Ag···Ag interactions are kept in the crystal, showing Ag−Ag distances of 2.9169(6) and 3.0958(7) Å, and the gold center is linearly coordinated to a mesityl group and to a tht ligand with Au−C and Au−S bond distances of 2.044(6) and 2.3423(16) Å. The latter is nearly identical to the Au−S bond length of 2.347(2) Å described for complex **4**, although in complex **6** the tetrahydrothiophene molecule acts as terminal instead of as bridging ligand. It is longer than in the complexes with gold(I) bonded to a terminal tht (2.237−2.335(6) Å)[12] and even longer than in **3** (2.3195(11) Å), in which tht bridges two metals.

As in the crystal structure of **3**, the *ipso* carbon of the mesityl ligand interestingly bridges one gold and two silver centers, being, together with complex **3**, the first examples of an *ipso* carbon atom bridging three transition metal centers. As in **3**, this should imply a longer Au−C distance than in **4** or in other compounds with aryl ligands bridging two instead of three metals.[3] In contrast, the Au−C distance in **6** (2.044(6) Å) shows again a stronger interaction than in the previously described complexes with aryl bridging ligands (Au−C distances in the range 2.067(7)−2.200(7) Å)[3] and of the same order as in compounds **3** (2.045(4) Å) and **4** (2.047(8) Å). Regarding the Ag−C distances, one of them (2.588(6) Å) compares well with the Ag−C lengths found in complexes **3** and **4** and is longer than the second one (2.385(6) Å), which is closer to those described for the related complexes $[\{(Ph_3P)Au(\mu\text{-mes})Ag(tht)\}_2][SO_3CF_3]_2$[3a] (2.326(3) Å), $[\{Au(\mu\text{-mes})(AsPh_3)\}_2Ag]ClO_4$[3b] (2.27(2) Å), $[Au_2Ag_2(C_6F_5)_4(OCMe_2)_2]_n$[3d] (2.440(8) and 2.506(8) Å), and $[NBu_4]_2[AuAg_4(3,5\text{-}C_6F_3Cl_2)_2(CF_3CO_2)_5]$[3e] (2.450(6) and 2.439(6) Å), all of them containing aryl bridging groups.

As mentioned in the Introduction, we were interested in the study of the factors that can influence the maintenance of the cyclic core $[Ag(\mu\text{-O,O}'\text{-RCO}_2)]_2$ in the complexes obtained by reaction of mesitylgold(I) with silver(I) perfluorocarboxylate, the reason for which we carried out the reaction in the presence or absence of a neutral donor ligand, such as tht or water, and with different solvents and molar ratios. We have seen that complexes **3**−**6** (in which the dimeric unit $[Ag(\mu\text{-}O,O'\text{-RCO}_2)]_2$ is kept) are obtained only if dichloromethane is employed as solvent, and there is no water present, in a 1:4 molar ratio and in the presence of 1 (**3** and **4**) or 3 (**5** and **6**) equiv of tht. On the other hand, when the reaction is carried out in different molar ratios of the reagents, when donor solvents, such as acetone or tetrahydrofuran, are employed, or when the solvent is not distilled and dehydrated, the resulting product is always the dark green complex $[AuAg(mes)(CF_3CO_2)]$ (**2**). Unfortunately, we have not been able to obtain single crystals of this compound that could allow us to know if the dimer $[Ag(RCO_2)]_2$ is also present in its solid state structure.

Finally, we tried to study the influence of water in the reaction and in the solid structure of the resulting complexes in order to know if complex **2** is formed if water is present in the reaction medium. Thus, we treated complexes **3**−**6** with water in different molar ratios, but in all the cases the reaction always leads to a green solution, which in the case of trifluoroacetate derivatives contains compound **2**, with a unique exception: when **3** is treated with water in a 1:2 molar ratio, the color of the solution turns orange and the new complex $\{[AuAg_4(mes)(CF_3CO_2)_4(tht)(H_2O)]\cdot H_2O\cdot CH_2Cl_2\}_n$ (**7**) is isolated as a dark orange solid (Scheme 1). This implies the incorporation of two molecules of water in the starting material (**3**), which is confirmed by its analytical and spectroscopic properties. Thus, its FT-IR spectrum shows, besides the bands arising from tht, mes, and trifluoroacetate, an absorption at 3429 cm^{-1}, due to the water that has been incorporated. The presence of these additional molecules of water is also detected in the ^1H NMR spectrum of **7**, showing a broad signal at 1.54 ppm, corresponding to water, in addition to the resonances due to the methylenic hydrogen atoms of the tetrahydrothiophene, the protons of the mesityl group, and those of the molecule of dichloromethane. It is worth noting that there is no significant shift of the resonances corresponding to mesityl and tht compared to those of the starting complex **3**. Regarding the ^{19}F NMR spectrum of **7**, as in **3** it shows a unique singlet at −73.5 ppm, which suggests the equivalence of all the trifluoroacetate anions in solution. Finally, the mass spectrum (ES-) suggests the presence of one molecule of water coordinated to silver, displaying peaks at *m*/*z* 334 and 662, corresponding to the fragments $[Ag(CF_3CO_2)_2]^-$ and $[Ag_2(CF_3CO_2)_3(tht)(OH_2)]^-$, respectively.

To unequivocally establish the structure of compound **7** in the solid state, single crystals suitable for X-ray diffraction study

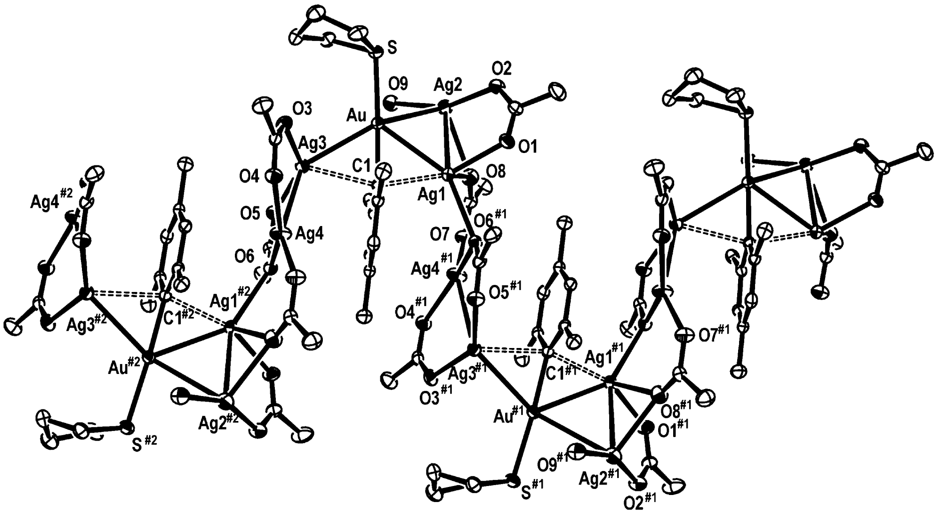

Figure 9. Part of the polymeric structure of complex **7** with the labeling scheme of the atom positions. Hydrogen and fluorine atoms have been omitted for clarity.

were obtained by layering a solution of **7** in dichloromethane with hexane. As in complexes **3**, **4**, and **6** the asymmetric unit contains a $[Ag_2(\mu\text{-}CF_3CO_2)_2]$ dimer and a [Au(mes)(tht)] unit, but shows a noticeable difference: in the second $[Ag_2(CF_3CO_2)_2]$ fragment the eight-membered cycle is no longer present. This is probably caused by the coordination of one molecule of water to one of the Ag^I centers with a bond distance of 2.195(5) Å, which is the shortest Ag−O length found in **7**. Thus, while one trifluoroacetate keeps its normal μ-η^2 coordination mode with Ag−O bond distances of 2.248(5) and 2.210(5) Å, the second one acts as a μ_3-η^2 ligand with O(8) bonded to Ag(1) and Ag(2), showing longer Ag−O bond lengths (2.420(6) and 2.488(6) Å), while O(7) binds to a Ag^I center of a neighboring $[Ag_2(\mu\text{-}CF_3CO_2)_2]$ dimer (Ag−O 2.336(6) Å). As in the structures described above, the fragments contained in the asymmetric unit, $[Ag_2(\mu\text{-}CF_3CO_2)_2]$, [Au(mes)(tht)], and $[Ag_2(\mu\text{-}CF_3CO_2)(\mu_3\text{-}\eta^2\text{-}CF_3CO_2)(OH_2)]$, are connected via Au···Ag and Ag···C short contacts, as shown in Figure 9. As in complex **6**, there are three Au···Ag contacts of 2.8503(6), 2.8708(6), and 3.1347(7) Å, the latter being the longest described to date in complexes containing aryl bridging ligands between Au^I and Ag^I (2.7758(8)−3.0134(6) Å),[3] while the other two Au−Ag lengths are close to those in complex **6** (2.8540(6) and 2.8845(6) Å).

The gold(I) atom is again almost linearly coordinated to a mesityl group and a tht ligand, and the *ipso* carbon of the mesityl ligand bridges one gold and two silver centers. Despite the presence of tht as a terminal ligand in **7**, the Au−S bond distance of 2.3386(19) Å is of the same order as in compounds **3** and **4** (2.3195(11) and 2.347(2) Å, respectively), in which the S-donor ligand bridges two metal centers, and longer than in other complexes with gold(I) bonded to a terminal tht (2.237−2.335(6) Å).[12] Regarding the Au−C bond distance of 2.063(7) Å, it compares well with those mentioned above for complexes **3**, **4**, and **6** (2.045(4), 2.047(8), and 2.044(6) Å) and is nearly identical to the Au−C distances described for $[NBu_4]_2[AuAg_4(3,5\text{-}C_6F_3Cl_2)_2(CF_3CO_2)_5]$[3e] (2.067(7) and 2.068(7) Å), all of them containing aryl bridging groups. The Ag−C bond lengths of 2.362(6) and 2.555(6) Å are similar to those described for **6** (2.385(6) and 2.588(6) Å), which displays a very similar bonding situation around the central $AuAg_2$ core.

Finally, another difference between the structures of **3**, **4** or **6**, and **7** is found in the mode of polymerization, which in **7** takes place through Ag−O contacts of 2.477(5) and 2.336(6) Å, resulting in a monodimensional polymer that runs parallel to the crystallographic *y* axis. As in the previous complexes **3**, **4**, and **6**, there are intramolecular Ag···Ag interactions in the crystal of 2.9725(8) and 3.0515(8) Å, the latter corresponding to the triply bridged pair of silver(I) centers Ag(1) and Ag(2).

In view of these results, we can conclude that the reaction of mesitylgold(I) with silver(I) perfluorocarboxylates leads to species containing Au···Ag interactions and keeping the dimeric cycle $[Ag_2(\mu\text{-}RCO_2)_2]$ only if the reaction is carried out in dichloromethane, the Au:Ag ratio is 1:4, and 1 or 3 mol of tht per mol of gold(I) is present. Under other conditions, such as the employment of different solvents or with dichloromethane that is not distilled and dried or treatment of the reagents in other molar ratios or in the absence of tht, a green solution is obtained, from which complex **2** can be identified in the derivatives with trifluoroacetate. Only the reaction of **3** with 2 mol of water leads to a different product, complex **7**, in which a partial breaking of the dimer is observed in the solid state, probably caused by the incorporation of water in the coordination sphere of one of the silver(I) atoms. We tentatively suggest that the presence of higher amounts of water or the use of a donor solvent could lead to the total break of the cycle, which seems to stabilize the systems.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Nicolet Nexus FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. C, H, S analysis were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were recorded on a HP59987 A Electrospray. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external) and $CFCl_3$ (^{19}F, external).

General Comments. Tetrahydrothiophene, silver trifluoroacetate, and silver pentafluoropropionate are commercially available and were purchased from Fluka and Aldrich. The precursor complex $[Au(\mu\text{-mesityl})]_5$[13] was obtained according to literature procedures.

Synthesis of $[Ag_4(CF_3CO_2)_4(tht)_2]$ (1). To a solution of $AgCF_3CO_2$ (0.088 g, 0.4 mmol) in dichloromethane (20 mL) was added tht (0.0199 g, 0.2 mmol). After 30 min of stirring the solution was concentrated in a vacuum to ca. 5 mL. Addition of *n*-hexane (10

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[13] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1304.

Table 1. Data Collection and Structure Refinement Details for Complexes 1, 3, 4, 6, and 7

	1	**3**	**4**	**6**	**7**
chemical formula	$C_{16}H_{16}Ag_4F_{12}O_8S_2$	$C_{21}H_{19}Ag_4AuF_{12}O_8S$	$C_{25}H_{19}Ag_4AuF_{20}O_8S$	$C_{33}H_{35}Ag_4Au$-$F_{20}O_8S_3$	$C_{21}H_{21}Ag_4Au$-$F_{12}O_9S{\cdot}H_2O{\cdot}CH_2C_{l2}$
cryst habit	colorless prism	yellow prism	yellow prism	yellow prism	dark orange prism
cryst size/mm	0.18 × 0.12 × 0.12	0.35 × 0.2 × 0.15	0.2 × 0.15 × 0.1	0.27 × 0.25 × 0.2	0.35 × 0.25 × 0.18
cryst syst	tetragonal	monoclinic	triclinic	monoclinic	monoclinic
space group	$I4_1/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	12.9294(3)	12.7175(1)	9.0739(2)	17.4049(2)	12.7920(1)
b/Å	12.9294(3)	22.9632(3)	12.0061(3)	13.2287(2)	12.7632(2)
c/Å	17.3000(6)	11.4802(1)	17.3606(4)	21.8433(3)	23.0315(3)
α/deg	90	90	93.971(14)	90	90
β/deg	90	111.473(1)	91.261(13)	106.5940(10)	105.6203(8)
γ/deg	90	90	99.875(8)	90	90
U/Å^3	2892.03(14)	3119.91(5)	1857.70(8)	4819.83(11)	3621.40(8)
Z	4	4	2	4	4
D_c/g cm^{-3}	2.434	2.742	2.660	2.293	2.584
M	1059.89	1287.87	1487.91	1664.24	1408.83
F(000)	2016	2400	1392	3168	2648
T/°C	−100	−100	−100	−100	−100
$2\theta_{max}$/deg	56	56	56	56	54
μ(Mo Kα)/mm^{-1}	2.929	7.334	6.208	2.293	6.477
no. of reflns measd	6273	29 036	30 644	68 752	59 185
no. of unique reflns	1721	7410	8706	11 366	7630
R_{int}	0.0294	0.0423	0.0621	0.0661	0.0552
R^a ($I > 2\sigma(I)$)	0.0372	0.0302	0.0514	0.0448	0.0414
wR^b (F^2, all reflns)	0.0941	0.0620	0.1134	0.0852	0.1056
no. of params	96	454	535	625	472
no. of restraints	0	106	133	11	97
S^c	1.170	1.029	1.093	1.046	1.011
max. $\Delta\rho$/e Å^{-3}	2.145	2.682	2.868	2.623	2.782

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

mL) was added to precipitate complex **1** as a white solid. Yield: 0.0982 g (92.6%). Anal. Calcd for **1** ($C_{16}H_{16}Ag_4F_{12}O_{10}S_2$): C, 18.13; H, 1.52; S, 6.05. Found: C, 18.32; H, 1.55; S, 6.35. FT-IR (Nujol mulls): ν(tht) at 1263 cm^{-1}, ν(CF_3CO_2) at 1663 and 1209 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 3.13 (m, 8H, S−CH$_2$−C*H*$_2$−) and 2.07 ppm (m, 8H, S−C*H*$_2$−CH$_2$−). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −73.5 ppm (s, 12F, C*F*$_3$CO$_2$). (ES$^-$): *m*/*z* 333 [Ag(CF_3CO_2)$_2$]$^-$.

Synthesis of [AuAg(mes)(CF$_3$CO$_2$)] (2). To a dichloromethane solution (20 mL) of [Au(mes)] (0.065 g, 0.2 mmol) was added AgCF$_3$CO$_2$ (0.044 g, 0.2 mmol), and the mixture rapidly turned green. After 30 min of stirring, the solution was concentrated in a vacuum to ca. 5 mL, and addition of *n*-hexane (10 mL) led to the precipitation of complex **2** as a dark green solid. Yield: 0.098 g (91.2%). Anal. Calcd for **2** ($C_{11}H_{11}AgAuF_3O_2$): C, 24.60; H, 2.06. Found: C, 24.48; H, 1.93. FT-IR (Nujol mulls): ν(mes) at 1592 and 851 cm^{-1} and ν(CF_3CO_2) at 1658 and 1186 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 6.89 (s, 2H, *m*-H), 2.84 (s, 6H, *o*-Me), and 2.17 ppm (s, 3H, *p*-Me). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −73.2 ppm (s, 3F, C*F*$_3$CO$_2$). (ES$^-$): *m*/*z* 332.6 [Ag(CF_3CO_2)$_2$]$^-$, 870 [AuAg$_2$(mes)(CF_3CO_2)$_3$]$^-$.

Synthesis of [AuAg$_4$(mes)(CF$_3$CO$_2$)$_4$(tht)]$_n$ (3). This product can be obtained by two alternative methods. Method 1: To a dichloromethane solution (20 mL) of [Au(mes)] (0.063 g, 0.2 mmol) was added complex **1** (0.106 g, 0.2 mmol). After 30 min of stirring, the solution was concentrated in a vacuum to ca. 5 mL. Addition of *n*-hexane (20 mL) led to the precipitation of **3** as a pale yellow solid, which was filtered and washed with *n*-hexane (2 × 5 mL) in order to remove the remaining tht. Yield: 0.232 g (90.1%).

Method 2: A dichloromethane solution (20 mL) of [Au(mes)] (0.063 g, 0.2 mmol) was treated with AgCF$_3$CO$_2$ (0.177 g, 0.8 mmol), and then tht (0.018 mL, 0.2 mmol) was added. The solution was stirred for 30 min, and further concentration in a vacuum and addition of 20 mL of *n*-hexane led to the precipitation of **3** as a pale yellow solid. Yield: 0.243 g (94.3%). Anal. Calcd for **3** ($C_{21}H_{19}Ag_4AuF_{12}O_8S$): C, 19.58; H, 1.49; S, 2.49. Found: C, 19.78; H, 1.61; S, 2.53. FT-IR (Nujol mulls): ν(tht) at 1264 cm^{-1}, ν(mes) at 847 cm^{-1}, and ν(CF_3CO_2) at 1663 and 1209 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 6.98 (s, 2H, *m*-H), 3.13 (m, 4H, S−CH$_2$−C*H*$_2$−), 2.47 (s, 6H, *o*-Me), 2.30 (s, 3H, *p*-Me), and 2.07 ppm (m, 4H, S−C*H*$_2$−CH$_2$−). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −73.5 ppm (s, 12F, C*F*$_3$CO$_2$). (ES$^-$): *m*/*z* 775 [Ag$_3$(CF_3CO_2)$_4$]$^-$, 870 [AuAg$_2$(mes)(CF_3CO_2)$_3$]$^-$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex 1[a]

Ag−O(1)	2.192(3)	Ag−O(2)	2.416(3)
Ag−S	2.4421(8)	Ag−Ag#1	3.2856(5)
O(1)−Ag−O(2)	110.49(10)	O(1)−Ag−S	153.02(8)
O(2)−Ag−S	96.41(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $y-1/4$, $-x+1/4$, $-z+1/4$

Synthesis of [AuAg$_4$(mes)(CF$_3$CF$_2$CO$_2$)$_4$(tht)]$_n$ (4). A dichloromethane solution (20 mL) of [Au(mes)] (0.063 g, 0.2 mmol) was treated with AgCF$_3$CF$_2$CO$_2$ (0.216 g, 0.8 mmol), and then tht (0.018 mL, 0.2 mmol) was added. The solution was stirred for 30 min, and further concentration in a vacuum and addition of 20 mL of *n*-hexane led to the precipitation of **4** as a pale yellow solid. Yield: 0.271 g (91.2%). Anal. Calcd for **4** ($C_{25}H_{19}Ag_4AuF_{20}O_8S$): C, 20.18; H, 1.29; S, 2.15. Found: C, 20.23; H, 1.22; S, 2.85. FT-IR (Nujol mulls): ν(tht) at 1258 cm^{-1}, ν(mes) at 855 cm^{-1}, and ν($CF_3CF_2CO_2$) at 1630 and 1217 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 7.00 (s, 2H, *m*-H), 3.16 (m, 4H, S−CH$_2$−C*H*$_2$−), 2.46 (s, 6H, *o*-Me), 2.32 (s, 3H, *p*-Me), and 2.10 ppm (m, 4H, S−C*H*$_2$−CH$_2$−). ^{19}F NMR (282.4 MHz, $CDCl_3$): −118.8 (s, 8F, CF$_3$C*F*$_2$CO$_2$) and −83.2 ppm (s, 12F, C*F*$_3$CF$_2$CO$_2$). (ES-) *m*/*z*: 433 [Ag($CF_3CF_2CO_2$)$_2$]$^-$, 704 [Ag$_2$($CF_3CF_2CO_2$)$_3$]$^-$, 977 [Ag$_3$($CF_3CF_2CO_2$)$_4$]$^-$.

Synthesis of [AuAg$_4$(mes)(CF$_3$CO$_2$)$_4$(tht)$_3$]$_n$ (5). To a solution of [Au(mes)] (0.063 g, 0.2 mmol) in dichloromethane (20 mL) were added AgCF$_3$CO$_2$ (0.177 g, 0.8 mmol) and tht (0.054 mL, 0.6 mmol). After 30 min of stirring the solution was concentrated in a vacuum to ca. 5 mL, and hexane (20 mL) was added to precipitate complex **5** as a pale yellow solid (0.204 g, 69.8%). Anal. Calcd

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Complex 3[a]

Au−C(1)	2.045(4)	Ag(3)−O(7)	2.281(3)
Au−S	2.3195(11)	Ag(3)−O(5)	2.367(3)
Au−Ag(1)	2.8226(4)	Ag(3)−O(8)#2	2.516(3)
Au−Ag(3)	2.8993(4)	Ag(2)−O(4)	2.207(3)
Ag(1)−Ag(2)	2.9149(5)	Ag(2)−O(2)	2.283(3)
Ag(3)−Ag(4)	2.9754(5)	Ag(2)−O(2)#3	2.429(3)
Ag(1)−S#1	2.6877(11)	Ag(4)−O(6)	2.151(3)
Ag(1)−C(1)	2.614(4)	Ag(4)−O(8)	2.208(3)
Ag(3)−C(1)	2.530(4)	Ag(4)−O(5)#4	2.518(3)
Ag(1)−O(3)	2.278(3)	Ag(3)−O(7)	2.281(3)
C(1)−Au−S	172.15(11)	S#1−Ag(1)−Au	106.38(3)
		Au−S−Ag(1)#1	118.17(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+1, −*y*+2, −*z*; #2 *x*, −*y*+3/2, *z*−1/2; #3 −*x*+2, −*y*+2, −*z*+1; #4 *x*, −*y*+3/2, *z*+1/2.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for Complex 4[a]

Au−C(1)	2.047(8)	Ag(1)−O(1)	2.221(6)
Au−S(1)	2.347(2)	Ag(2)−O(2)	2.239(6)
Au−Ag(3)	2.8140(8)	Ag(2)−O(3)	2.324(6)
Au−Ag(1)	2.8166(8)	Ag(2)−O(7)#2	2.408(6)
Ag(1)−Ag(2)	2.9479(10)	Ag(3)−O(5)	2.286(6)
Ag(3)−Ag(4)	2.9295(10)	Ag(3)−O(7)	2.367(6)
Ag(1)−S(1)#1	2.888(2)	Ag(3)−O(3)#3	2.532(6)
Ag(3)−C(1)	2.532(8)	Ag(4)−O(8)	2.196(7)
Ag(2)−C(5)	2.650(8)	Ag(4)−O(6)	2.248(6)
Ag(1)−O(4)	2.218(6)	Ag(4)−O(6)#4	2.417(6)
C(1)−Au−S(1)	174.1(2)	Au−Ag(1)−S(1)#1	88.01(5)
S(1)−Au−Ag(1)	108.88(6)	Au−S(1)−Ag(1)#1	138.60(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+1, −*y*+1, −*z*+1; #2 *x*+1, *y*, *z*; #3 *x*−1, *y*, *z*; #4 −*x*+1, −*y*+1, −*z*.

Table 5. Selected Bond Lengths [Å] and Angles [deg] for Complex 6[a]

Au−C(1)	2.044(6)	Ag(2)−C(1)	2.385(6)
Au−S(1)	2.3423(16)	Ag(3)−C(1)	2.588(6)
Au−Ag(1)	2.8540(6)	Ag(1)−O(4)	2.240(4)
Au−Ag(3)	2.8845(6)	Ag(1)−O(1)	2.277(5)
Au−Ag(2)	3.0782(6)	Ag(2)−O(2)	2.295(4)
Ag(1)−Ag(2)	2.9169(6)	Ag(2)−O(3)	2.328(4)
Ag(3)−Ag(4)	3.0958(7)	Ag(3)−O(5)	2.283(5)
Ag(1)−S(2)	2.6295(16)	Ag(3)−O(7)	2.292(4)
Ag(2)−S(3)	2.7116(17)	Ag(4)−O(8)	2.200(5)
Ag(3)−S(2)#1	2.7226(16)	Ag(4)−O(6)	2.215(5)
Ag(4)−S(3)#2	2.6574(17)		
C(1)−Au−S(1)	173.00(17)	S(2)−Ag(1)−Au	119.70(4)
Ag(1)−Au−Ag(3)	150.891(16)	S(2)#1−Ag(3)−Au	88.76(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+2, −*y*+1, −*z*+1; #2 −*x*+3/2, *y*+1/2, −*z*+3/2.

Table 6. Selected Bond Lengths [Å] and Angles [deg] for Complex 7[a]

Au−C(1)	2.063(7)	Ag(1)−O(8)	2.420(6)
Au−S	2.3386(19)	Ag(1)−O(6)#1	2.477(5)
Au−Ag(1)	2.8503(6)	Ag(2)−O(9)	2.195(5)
Au−Ag(3)	2.8708(6)	Ag(2)−O(2)	2.210(5)
Au−Ag(2)	3.1347(7)	Ag(2)−O(8)	2.488(6)
Ag(1)−Ag(2)	3.0515(8)	Ag(3)−O(3)	2.243(5)
Ag(3)−Ag(4)	2.9725(8)	Ag(3)−O(5)	2.254(5)
Ag(1)−C(1)	2.362(6)	Ag(4)−O(6)	2.244(5)
Ag(3)−C(1)	2.555(6)	Ag(4)−O(4)	2.256(5)
Ag(1)−O(1)	2.248(5)	Ag(4)−O(7)#2	2.336(6)
C(1)−Au−S	174.84(17)	Ag(3)−Au−Ag(2)	143.726(18)
Ag(1)−Au−Ag(3)	114.358(18)	Au−Ag(3)−Ag(4)	129.43(2)
Ag(1)−Au−Ag(2)	61.091(16)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+1, *y*+1/2, −*z*+1/2; #2 −*x*+1, *y*−1/2, −*z*+1/2.

for **5** ($C_{29}H_{35}Ag_4AuF_{12}O_8S_3$): C, 23.79; H, 2.41; S, 6.57. Found: C, 23.69; H, 2.15; S, 7.19. FT-IR (Nujol mulls): ν(tht) at 1265 cm^{-1}, ν(mes) at 893 cm^{-1}, and $\nu(CF_3CO_2)$ at 1650 and 1211 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 6.99 (s, 2H, *m*-H), 3.22 (m, 12H, $S-CH_2-CH_2-$), 2.49 (s, 6H, *o*-Me), 2.31 (s, 3H, *p*-Me), and 2.11 ppm (m, 12H, $S-CH_2-CH_2-$). ^{19}F NMR (282.4 MHz, $CDCl_3$): −73.6 ppm (s, 12F, CF_3CO_2). (ES$^-$) *m*/*z*: 333 $[Ag(CF_3CO_2)_2]^-$, 554 $[Ag_2(CF_3CO_2)_3]^-$.

Synthesis of $[AuAg_4(mes)(CF_3CF_2CO_2)_4(tht)_3]_n$ (6). To a solution of [Au(mes)] (0.063 g, 0.2 mmol) in 20 mL of dichloromethane were added $AgCF_3CF_2CO_2$ (0.217 g, 0.8 mmol) and tht (0.054 mL, 0.6 mmol), and the mixture was stirred for 30 min. The solution was then concentrated in a vacuum, and 20 mL of hexane was added to precipitate complex **6** as a pale yellow solid (0.376 g, 74.4%). Anal. Calcd for **6** ($C_{33}H_{35}Ag_4AuF_{20}O_8S_3$): C, 23.81; H, 2.12; S, 5.78. Found: C, 23.33; H, 2.10; S, 5.39. FT-IR (Nujol mulls): ν(tht) at 1260 cm^{-1}, ν(mes) at 891 cm^{-1}, and $\nu(CF_3CF_2CO_2)$ at 1649 and 1214 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 7.00 (s, 2H, *m*-H), 3.15 (m, 12H, $S-CH_2-CH_2-$), 2.46 (s, 6H, *o*-Me), 2.31 (s, 3H, *p*-Me), and 2.10 ppm (m, 12H, $S-CH_2-CH_2-$). ^{19}F NMR (282.4 MHz, $CDCl_3$): −83.2 (s, 8F, $CF_3CF_2CO_2$) and −118.9 ppm (s, 12F, $CF_3CF_2CO_2$). (ES$^-$) *m*/*z*: 433 $[Ag(CF_3CF_2CO_2)_2]^-$, 704 $[Ag_2(CF_3CF_2CO_2)_3]^-$.

Synthesis of $\{[AuAg_4(mes)(CF_3CO_2)_4(tht)(H_2O)]\cdot H_2O\cdot CH_2Cl_2\}_n$ (7). Complex **3** (0.257 g, 0.2 mmol) was dissolved in 20 mL of dichloromethane, and water (10 μL, 0.4 mmol) was added. The solution, which rapidly turned orange, was stirred for 15 min, and further evaporation of the solvent gave complex **7** as a dark orange solid (0.106 g, 40.6%). Anal. Calcd for **7** ($C_{22}H_{25}Ag_4AuCl_2F_{12}O_{10}S$): C, 18.54; H, 1.77; S, 2.25. Found: C, 18.81; H 1.71; S, 2.38. FT-IR (Nujol mulls): $\nu(H_2O)$ at 3429 cm^{-1}, ν(tht) at 1258 cm^{-1}, ν(mes) at 846 cm^{-1}, and $\nu(CF_3CO_2)$ at 1653 and 1184 cm^{-1}. ^{1}H NMR (75.5 MHz, $CDCl_3$): δ 7.05 (s, 2H, *m*-H), 5.29 (s, 2H, CH_2Cl_2), 3.19 (m, 4H, $S-CH_2-CH_2-$), 2.47 (s, 6H, *o*-Me), 2.35 (s, 3H, *p*-Me), 2.14 (m, 4H, $S-CH_2-CH_2-$), and 1.54 ppm (m, 4H, H_2O). ^{19}F NMR (282.4 MHz, $CDCl_3$): −73.5 ppm (s, 12F, CF_3CO_2). (ES$^-$) *m*/*z*: 334 $[Ag(CF_3CO_2)_2]^-$, 662 $[Ag_2(CF_3CO_2)_3(tht)(OH_2)]^-$.

Crystallography. The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected by monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type: ω and ϕ. Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.[14] All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included using a mixed model. Further details on the data collection and refinement methods can be found in Table 1. Selected bond lengths and angles are shown in Tables 2−6, and crystal structures of **1**, **3**, **4**, **6**, and **7** can be seen in Figures 1−9. CCDC-606941−606945 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Figures S1−4 show the packing of complexes **3**, **4**, **6**, and **7** in the solid state. This material can be obtained, free of charge, via the Internet at http://pubs.acs.org.

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(14) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.