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A Cyclic Hexamer of Silver Trifluoroacetate Supported by Four Triphenylphosphine Sulfide Template Molecules

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Crystallization of silver trifluoroacetate from chloroform solutions containing triphenylphosphine sulfide affords a trigonal and a monoclinic form of a 6:4 complex $\{[CF_3C(O)OAg]_6(Ph_3PS)_4\}$ of C_2 symmetry with different amounts of chloroform in the crystals. With the Ph_3PS components as template molecules, the $CF_3C(O)OAg$ units are assembled to form a 6-membered metallacycle codetermined by metallophilic bonding and enclosed by a 24-membered ring $[AgOCO]_6$. A complex of the type $[LAgOC(O)CF_3]_2$, with L representing the isocyanide ligand $^{p}TolSO_2$-CH_2NC, has been shown to have a conventional bicyclic structure with three-coordinate silver atoms engaged in transannular metallophilic interactions.

Introduction

Silver(I) carboxylates $[AgOC(O)R]_n$ with no auxiliary donor ligands have been shown to form oligomers with a variety of structural motifs including mainly dimers with flat eight-membered rings **A**[1−3] or tetramers with folded 16-membered rings **B**,[4] the geometry of which is clearly codetermined by metallophilic bonding between the linearly two-coordinate metal atoms (Chart 1). Because of this low degree of aggregation, silver carboxylates with small non-polarizable substituents (such as perfluoroalkyl $-C_nF_{2n+1}$) are volatile in a vacuum and can be employed as sources for the chemical vapor deposition of silver metal.[5−8]

With donor ligands L, the ring systems of 1:1 complexes $[(L)AgOC(O)R]_n$ and 1:2 complexes $[(L)_2AgOC(O)R]_n$ can remain intact with the coordination number (CN) of the metal atoms increasing to 3 or 4, preserving metallophilic bonding as in **C**[8,9] or losing the Ag---Ag contacts as in **D** (Chart 1).[10] The literature is particularly rich in examples with L = tertiary phosphines or arsines.[5−17]

It should be noted that the structural chemistry of the silver carboxylates is entirely different from that of the corresponding gold carboxylates, where complexes of the type [(L)-AuOC(O)R] are generally monomers with the gold atoms linearly two-coordinate with complementary aurophilic bonding in a T-shaped geometry for small ligands L.[18−23] Only

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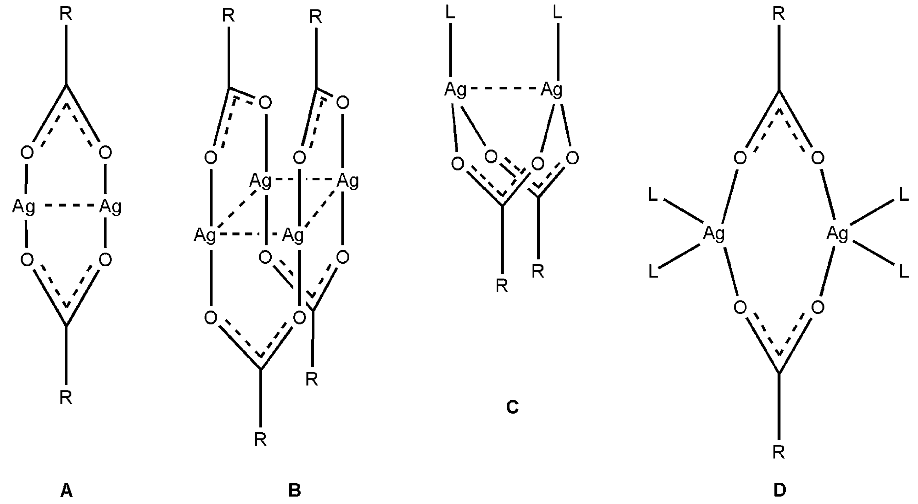
10.1021/ic048795o CCC: $30.25

Chart 1



A B C D

large ligands L may prevent the close approach necessary for bonding Au---Au contacts.

Results

An illustrative example for the standard behavior of the 1:1 complexes with an auxiliary ligand taken from the isocyanide series is presented here as a reference. The reaction between silver(I) trifluoroacetate and *p*-tolylsulfonylmethyl isocyanide (in chloroform) affords high yields of a colorless product $\{(^{p}TolSO_2CH_2NC)Ag[OC(O)CF_3]\}_2$ (**1**). The structure of type **C** shown in Figure 1 approaches C_2 symmetry quite closely and features a metallophilic Ag---Ag contact of 3.0213(4) Å between silver atoms which are in a planar three-coordinate configuration.

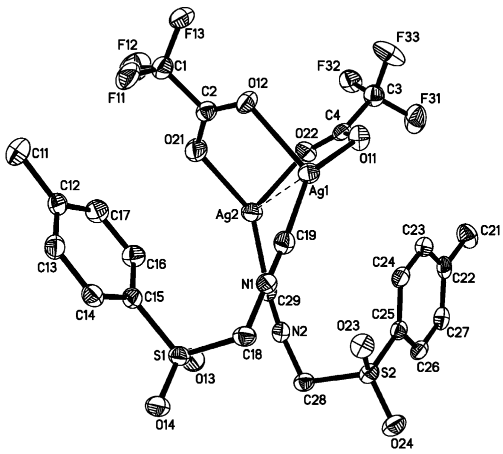


Figure 1. Molecular structure of $[^{p}TolSO_2CH_2NCAgOC(O)CF_3]_2$ (**1**) (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). The structure approaches C_2 symmetry, the virtual 2-fold axis passing through the midpoint of the lines connecting the atoms Ag1 with Ag2 and N1 with N2. Bond distances and angles show no anomalies.

By contrast, the reaction of $AgOC(O)CF_3$ with triphenylphosphine sulfide, also in a 1:1 molar ratio, gives a colorless 3:2 adduct of the components which crystallizes from chloroform as pentane vapor is allowed to diffuse into solution. With only slight variations of the experimental conditions, which presently cannot really be specified, crops of crystals were obtained which contained various amounts of two crystalline phases which could be identified as different solvates containing the same hexanuclear species of the formula $\{(Ph_3PS)_4\cdot[AgOC(O)CF_3]_6\}$ (**2**). Vacuum-dried solvent-free samples (54% yield, mp 167 °C dec) have been characterized by elemental analysis and NMR spectroscopy. Only one set of ^{1}H and ^{13}C resonances and a ^{31}P singlet (δ 46.8 ppm) were obtained for the four Ph_3PS ligands, while the equivalence of the six CF_3CO_2 units was demonstrated by a ^{19}F singlet (δ −73.4 ppm).

Crystals of compound **2** are either trigonal (with a huge unit cell, $Z = 18$) or monoclinic ($Z = 8$), with space groups *R*3c and *C*2/*c*, respectively. In both phases, which differ only in their ill-defined contents of solvent molecules, complex **2** has crystallographically imposed C_2 symmetry. The geometries are very similar, and therefore, only the structure of the molecules in the *trigonal* form is presented and discussed in detail here.

The structure is best described as an extension of the series started in formulas **A** and **B**: Following an 8- and a 16-membered ring, a 24-membered ring assembled of six silver atoms and six carboxylate OCO units is discernible, and in this macrocycle the six silver atoms are connected via metallophilic (argentophilic) bonding to give a 6-membered metallacycle in a twisted boat conformation (Figures 2 and 3). The average Ag---Ag contact is 3.020 Å. Six corner-sharing five-membered rings CO_2Ag_2 are annelated to the metallacycle, two roughly in the best plane defined by the silver atoms, two above, and two below.

Two pairs of triphenylphosphine sulfide molecules occupy symmetrical positions relative to the 2-fold axis above and below the macrocycle. Their sulfur atoms cap triangles of silver atoms (S1 for Ag2,Ag1,Ag3* and S2 for Ag1,Ag2, Ag3), providing each silver atom with two Ag−S contacts in addition to its two Ag−O contacts (Figure 4). The silver atoms thus become four-coordinate (AgO_2S_2) in a quasi-

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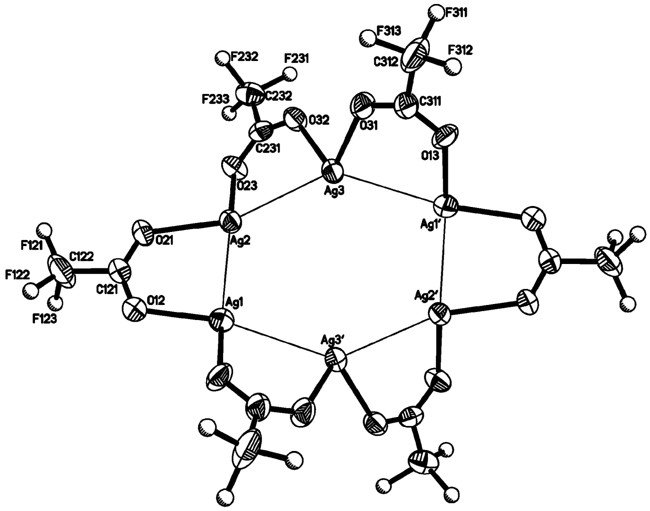

Figure 2. Hexanuclear subunit $(CF_3CO_2Ag)_6$ of the complex $[(Ph_3PS)_4\cdot(CF_3CO_2Ag)_6]$ (**2**) in the trigonal crystals (ORTEP, 50% probability ellipsoids except for fluorine atoms, hydrogen atoms omitted). The projection follows the C_2 axis passing through the center of the macrocycle.

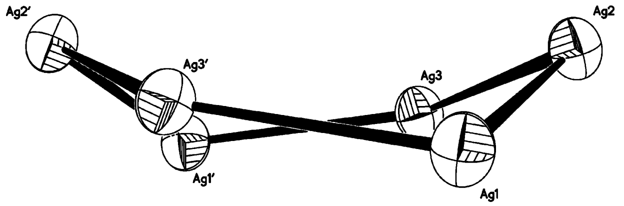

Figure 3. Twisted boat form of the central metallacycle of compound **2** (point group C_2 symmetry). The interatomic distances are Ag1−Ag2 = 2.9133(6) Å, Ag2−Ag3 = 3.0464(6) Å, and Ag3−Ag1′ = 3.1001(6) Å.

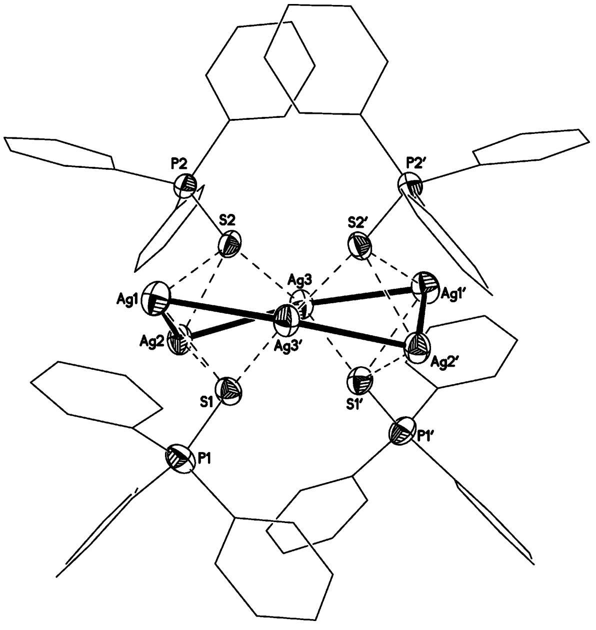

Figure 4. Subunit $[(Ph_3PS)_4Ag_6]$ (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted) showing the positions of the sulfur atoms above and below the metallacycle. Each silver atom is coordinated to two sulfur atoms and each sulfur atom to three silver atoms. The projection runs perpendicular to the C_2 axis, which passes through the midpoint of the line connecting the atoms Ag3 and Ag3′.

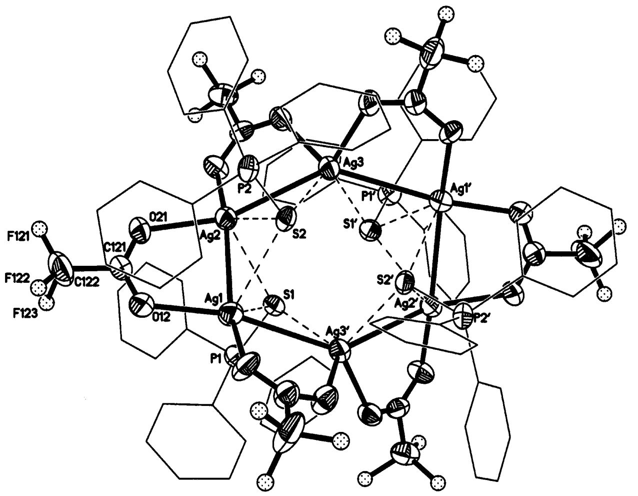

Figure 5. Complete structure of complex **2** (ORTEP, 50% probability ellipsoids except for phenyl carbon atoms and fluorine atoms, hydrogen atoms omitted).

tetrahedral geometry with the Ag−S and Ag−O bond lengths in broad ranges from 2.5426 to 2.8769 Å and from 2.248 to 2.326 Å, respectively, and entertain two metallophilic contacts (Figure 5). Phosphine sulfide coordination to silver(I) atoms has been observed previously,[24−26] but no μ^3-coordination has been reported.

It appears that the Ph_3PS molecules are templates for the formation of the hexamer of silver trifluoroacetate. They provide an exposed sulfur atom which can function as a donor center for three neighboring silver centers. With the sulfur atoms capping two different silver triples, all six silver atoms can reach CN 4 with only four Ph_3PS ligands, which explains the 6:4 stoichiometry. This compact array is obviously a preferred mode of organization which has the same structure regardless of the number and distribution of solvent molecules in the two different crystalline solvates.

The NMR data for chloroform solutions at 20 °C indicate that the hexanuclear aggregate enjoys great fluxionality in solution, which renders the trifluoroacetate and the triphenylphosphine sulfide ligands equivalent on the NMR time scale. Cooling of samples to the solubility limit (ca. −50 °C) did not lead to line broadening or splitting of the ^{19}F and ^{31}P signals which are to be expected for a rigid structure with C_2 symmetry. This result suggests that the Ph_3PS ligands can undergo facile intra- or intermolecular “ring hopping”, meaning that they can move freely to other silver triangles with concomitant flapping of the five-membered CO_2Ag_2 rings. Moreover, there can be flapping of the six-membered ring of silver atoms (Figure 3). However, dissociative mechanisms also cannot be excluded. Substitution of the Ph_3PS units by strong donor ligands (phosphines, isocyanides) leads to conventional complexes of other $[(L)_n(CF_3CO_2Ag]_m$ oligomers.

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Table 1. Crystal Data, Data Collection, and Structure Refinement Details for $[^pTolSO_2CH_2NCAgOC(O)CF_3]_2$ (**1**), $\{(Ph_3PS)_4{\cdot}[AgOC(O)CF_3]_6\}$ (**2**), and $\{(Ph_3PS)_4{\cdot}[AgOC(O)CF_3]_6\}{\cdot}(CHCl_3)_{0.87}$ (**2**)

	$[^pTolSO_2CH_2NCAg$-$OC(O)CF_3]_2$ (**1**)	$\{(Ph_3PS)_4{\cdot}[Ag$-$OC(O)CF_3]_6\}$ (**2**)	$\{(Ph_3PS)_4{\cdot}[AgOC(O)$-$CF_3]_6\}{\cdot}(CHCl_3)_{0.87}$ (**2**)
empirical formula	$C_{22}H_{18}Ag_2F_6N_2O_8S_2$	$C_{84}H_{60}Ag_6F_{18}$-$O_{12}P_4S_4$	$C_{84.87}H_{60.87}Ag_6Cl_{2.61}$-$F_{18}O_{12}P_4S_4$
fw	832.24	2502.66	2606.61
cryst syst	triclinic	trigonal	monoclinic
space group	$P\bar{1}$	$R\bar{3}c$	$C2/c$
a/Å	10.9501(3)	29.0992(2)	53.1396(6)
b/Å	11.2398(4)	29.0992(2)	15.1408(2)
c/Å	13.8195(4)	64.5822(6)	27.3641(4)
α/deg	104.2352(18)	90	90
β/deg	96.633(2)	90	120.4072(9)
γ/deg	118.9642(12)	120	90
V/Å^3	1386.14(7)	47359.3(6)	18988.1(4)
ρ_{calcd}/g cm^{-3}	1.994	1.579	1.824
Z	2	18	8
F(000)	816	22104	10228
μ(Mo Kα) (cm^{-1})	16.53	13.17	15.35
T/K	143	143	143
no. of reflns measured	39342	354127	274446
no. of unique reflns	4763 [$R_{int} = 0.043$]	9649 [$R_{int} = 0.099$]	16477 [$R_{int} = 0.063$]
no. of refined params/restraints	380/0	636/0	1190/0
R1 [$I \geq 2\sigma(I)$]	0.0297	0.0561	0.0423
wR2^a	0.0656	0.1146	0.0939
weighting scheme	$a = 0.0079$ $b = 2.0580$	$a = 0.0372$ $b = 401.0217$	$a = 0.0321$ $b = 94.7621$
σ_{fin}(max/min)/e Å^{-3}	0.427/−0.331	0.610/−0.806	1.090/−0.638

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

Experimental Section

Preparation of Complex 1. $^pTolSO_2CH_2NC$ (200 mg, 1.02 mmol) and CF_3CO_2Ag (226 mg, 1.02 mmol) were reacted in 10 mL of $CHCl_3$ at room temperature in the dark overnight. The reaction mixture was evaporated to dryness in a vacuum, the residue washed with diethyl ether, and dried in a vacuum to leave 352 mg of a colorless solid (83% yield, mp 164 °C dec). Anal. Found: C, 30.92; H, 2.11. Calcd for $C_{11}H_9AgF_3NO_4S$ (416.12): C, 31.75; H, 2.18. ^1H NMR ($CDCl_3$, 20 °C): δ 2.44, s, 3H, CH_3; 4.76, s, 2H, CH_2; 7.43 and 7.88, m, 2 × 2H, C_6H_4. $^{13}C\{^1H\}$ NMR: δ 21.7, s, CH_3; 61.9, s, CH_2; 129.2, 130.9, 132.3, and 148.1, C_6H_4; 163.0, br, NC. ^{19}F NMR: δ −74.3, s. MS (FAB): m/z 498 $[L_2Ag]^+$.

Preparation of Complex 2. A suspension of CF_3CO_2Ag (200 mg, 0.90 mmol) in 10 mL of dry $CHCl_3$ was treated with a solution of Ph_3PS (266 mg, 0.90 mmol) in another 10 mL of the same solvent at room temperature in the dark for 2 h. The solvent was subsequently removed in a vacuum, the residue extracted with pentane, and the colorless product crystallized from chloroform/pentane and dried in a vacuum (204 mg, 54% yield, mp 167 °C dec). Anal. Found: C, 41.67; H, 2.64. Calcd for $C_{42}H_{30}Ag_3F_9O_6P_2S_2$ (1251.35): C, 40.31; H, 2.42. ^1H NMR ($CDCl_3$, 20 °C): δ 7.71−7.43, m, Ph. $^{13}C\{^1H\}$ NMR: δ (for C^1−C^4, respectively) 128.6, d, $J = 88.2$ Hz; 129.6, d, $J = 11.9$ Hz; 132.5, d, $J = 10.4$; 133.6, s. $^{31}P\{^1H\}$ NMR: δ 46.8, s. ^{19}F NMR: δ −73.4 ppm. MS (FAB): m/z 697 $[L_2Ag]^+$. Crystals of **2**$\cdot(CHCl_3)_{0.87}$ were grown from chloroform/pentane.

Crystal Structure Determinations. Specimens of suitable quality and size were mounted onto the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP 2020 diffractometer, employing graphite-monochromated Mo Kα radiation. Intensity data were corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[27] The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. During the structure refinement of both crystalline phases of the compound $[(Ph_3PS)_4{\cdot}(CF_3CO_2Ag)_6]$ (**2**), the atoms of two chloroform molecules were observed. While in the trigonal case none could be modeled satisfactorily, one of two solvent molecules of the monoclinic form was refined but its site found to be not fully occupied (87%). The SQUEEZE routine in PLATON was used to modify the *hkl* files. Further information on crystal data, data collection, and structure refinement is summarized in Table 1.

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

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