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Article

Formation of Crystalline Polymers from the Reaction of Amine-Functionalized C_{60} with Silver Salts

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Three new crystalline compounds of Ag(I) with fullerene-containing ligands, the piperidine adduct $[C_{60}(N(CH_2CH_2)_2N)]$ and the fullero[60]pyrrolidine $[C_{60}(CH_2N(CH_3)CH_2)]$, have been prepared and characterized by X-ray crystallography. The polymeric structure of $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$ consists of linear chains composed of two distinct molecules of the functionalized fullerene, with four Ag(I) ions attached to the four nitrogen atoms and four bridging trifluoroacetate ions. Two of the four Ag(I) ions form η^2-bonds to carbon atoms in different regions of the fullerene cage, and there is one close Ag−Ag contact (3.1657(7) Å) as well. These chains are further cross-linked by bridging trifluoroacetate ions. The structure of $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\}\cdot 0.25CH_3OH$ involves two similar polymeric chains in which Ag(I) ions bind to the nitrogen atom of one *N*-methyl-3,4-fullero[60]pyrrolidine ligand and to a carbon atom of another *N*-methyl-3,4-fullero[60]pyrrolidine in η^1-fashion for one chain and in distorted η^2-fashion in the other. Additionally, each Ag(I) ion is bonded to two oxygen atoms from two bridging nitrate ions. On the other hand, $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$ is a simple coordination complex with two very large ligands attached to Ag(I). Coordination of Ag(I) to C_{60} produces much smaller alterations to the fullerene geometry than does coordination of $Pt^0(PPh_3)_2$ or $Ir^I(CO)Cl(PPh_3)_2$ groups.

Introduction

Ag(I) ions readily bind with olefins[1] and arenes,[2] but there have only been a few documented situations in which Ag(I) ions bind directly to fullerenes. The cations $[Ag_xC_{60}]^+$ ($x = 1-5$) and $[Ag(C_{60})_2]^+$ have been detected in the gas phase through mass spectroscopic studies.[3] It has been reported that addition of Ag(I) ions to solutions of C_{60} does not alter the electronic spectrum of C_{60}.[4] Fullerenes that have attached amino−ether groups show spectroscopic changes that were attributed to Ag^+-C_{60} π-bonded interactions.[5] Dark red, nearly black blocks of $C_{60}\{Ag(NO_3)\}_5$ were obtained by mixing solutions of silver nitrate and C_{60}.[6] This remarkable solid has a structure in which the silver nitrate portion forms a curved network that encapsulates the nearly spherical C_{60} molecules. In this solid, there are both η^1- and η^2-interactions of Ag(I) ion with the fullerene. Ag(II) porphyrins,[7] like many metalloporphyrins,[8] co-crystallize with C_{60} and are notable for the interactions between the two paramagnetic Ag(II) ions. Thermolysis of fullerenes in the presence of Ag(I) trifluoroacetate results in the addition of trifluoromethyl groups onto the fullerene outer surface.[9] Networks containing fullerenes have been prepared by the reaction of silver ions Ag(I) with fullerenes bearing pyridyl addends, but there is no direct coordination of the fullerene by Ag(I) ions in these networks.[10]

Here we report the synthesis and structural characterization of Ag(I) complexes of the two chemically modified fullerenes shown in Scheme 1. These modified fullerenes contain amine

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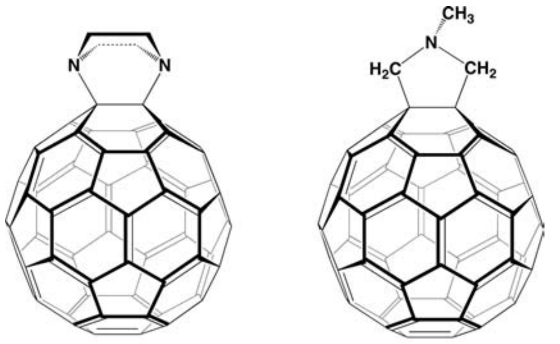
Scheme 1. Fullerene Adducts



$C_{60}(N(CH_2CH_2)_2N)$ $C_{60}(CH_2N(CH_3)CH_2)$

functionalities that are positioned near the fullerene surface. The basic tertiary amine groups provide primary sites for Ag(I) ion coordination, but the surface of the carbon cage is also available for coordination to Ag(I). The bifunctional nature of $C_{60}(N(CH_2CH_2)_2N)$ is especially appropriate for the formation of a polymeric material. Polymeric fullerenes containing metal centers are involved in the redox-active films that are formed by reducing C_{60} and certain transition metal complexes,[11,12] and it is useful to have crystalline models that show how such polymeric materials can be constructed. In constructing Ag(I) complexes with these modified fullerenes, the major problem was finding a solvent or solvent combination that allows the rather ionic Ag(I) salt to be mixed with the relatively nonpolar fullerene adduct.

Results and Discussion

Structural Results for $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$. Crystals of this complex were obtained through the slow evaporation of a mixture of a carbon disulfide solution of Ag(I) trifluoroacetate and a carbon disulfide solution of $C_{60}(N(CH_2CH_2)_2N)$. Small, thin, red-brown plates start to form within a few minutes after mixing. Suitable crystals that were large enough to provide suitable X-ray diffraction data were observed within 1 week. Crystallographic data are contained in Table 1. Once formed, we could not find a common organic solvent that would dissolve these crystals.

Crystalline $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$ forms a complex polymeric network. The asymmetric unit includes two molecules of the functionalized fullerene, two Ag(I) ions, four trifluoroacetate ions, one ordered carbon disulfide molecule, and another carbon disulfide molecule that is partitioned between two sites. Figure 1 shows a portion of the polymeric chain that extends infinitely along the horizontal direction.

There are a number of interesting features of this complicated unit. Each of the nitrogen atoms of the two functionalized fullerenes in the asymmetric unit is coordinated to a unique Ag(I) ion. The Ag−N distances are N1−Ag2#1, 2.357(4) Å; N2−Ag3, 2.317(4) Å; N3−Ag1, 2.368(4) Å; and N4−Ag4, 2.483(4) Å. However, each of the four Ag(I) ions displays its own distinct coordination geometry. Starting at the left in Figure 1, we see that Ag2 is η^2-coordinated to a fullerene cage with nearly equivalent Ag−C distances of 2.348(5) Å for C91 and 2.366(4) Å for C92. Additionally, Ag2 is attached to the oxygen atoms of two trifluoroacetate ions (Ag2−O6, 2.395(3) Å; Ag2−O7, 2.280(3) Å) and to N1C from an adjacent unit cell. One trifluoroacetate ion bridges Ag2 and Ag4. Ag4 is connected to N4 and to the oxygen atoms of three trifluoroacetate ions (Ag4−O5, 2.450(3) Å; Ag4−O5A, 2.337(3) Å; and Ag4−O8A, 2.279(3) Å) to form a roughly tetrahedral array. Ag1 and Ag3 are bridged by two trifluoroacetate ions with a Ag1···Ag3 separation of 3.1652(7) Å. The proximity of Ag1 and Ag3 suggests that there may be an argentophilic interaction between these two metal centers. Comparable Ag···Ag separations have been seen in cases where significant attractive interactions exist between the Ag(I) ions.[13−15] Ag1 is also coordinated to N3 and two carbon atoms of the adjoining fullerene in η^2-fashion (C13−Ag1, 2.403(4) Å; C30−Ag1, 2.430(5) Å). In addition to the attachment to Ag1 through the two bridging trifluoroacetate ions, Ag3 is connected to N2 and to an oxygen atom of a trifluoroacetate ion of an adjacent asymmetric unit.

The chains described above are linked through bridging via O3, as seen in Figure 2 that shows how two parallel strands of the polymer are interconnected. Notice that each

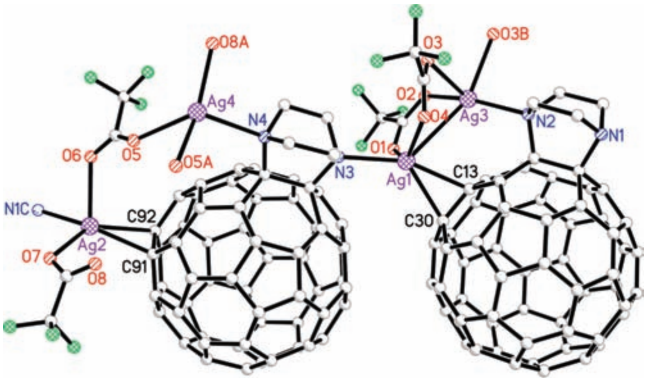


Figure 1. A portion of the structure of $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$. For clarity, the atoms are shown as arbitrarily sized circles and the carbon disulfide molecules and hydrogen atoms are omitted. The green circles are fluorine atoms, and the gray circles are carbon atoms.

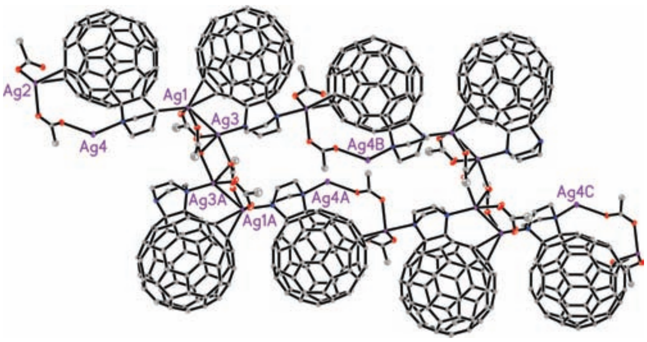


Figure 2. Drawing of two polymeric strands in $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$ that shows the bridging between the two strands. For clarity, the atoms are shown as arbitrarily sized circles and the carbon disulfide molecules, hydrogen atoms, and fluorine atoms are omitted.

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Table 1. Crystal Data and Data Collection Parameters

	$\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$	$[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$	$\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\}\cdot 0.25CH_3OH$
formula	$C_{69}H_8Ag_2F_6N_2O_4S_2$	$C_{129.50}H_{20}AgCl_2N_5O_{3.50}$	$C_{63.25}H_8AgN_2O_{3.25}$
formula weight	1322.63	1880.28	955.59
color, habit	brown plate	brown plate	red plate
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1$
a, Å	9.9780(18)	10.0274(10)	17.2057(15)
b, Å	19.413(4)	36.014(4)	9.9089(9)
c, Å	22.522(6)	18.9837(18)	19.4765(17)
α, deg	75.157(4)	90	90
β, deg	87.116(4)	103.923(2)	98.3707(19)
γ, deg	87.845(6)	90	90
V, Å^3	4210.3(16)	6654.1(12)	3285.2(5)
T, K	173(2)	100(2)	90(2)
Z	4	4	4
d_{calcd}, g$\cdot$cm^{-3}	2.087	1.877	1.932
radiation (λ, Å)	0.71073	0.71073	0.71073
μ, mm^{-1}	1.127	0.471	0.686
range of transm factors	0.70 to 0.99	0.86 to 0.99	0.81 to 0.99
unique data	18029	11611	12005
restraints	0	722	1
params refined	824	1274	606
R1[a]	0.048	0.060	0.065
wR2[b]	0.116	0.157	0.118

[a] For data with $I > 2\sigma I$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] For all data, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

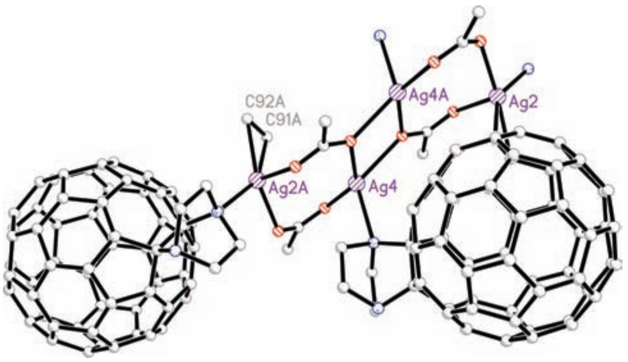

Figure 3. Drawing of a portion of $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$ showing the bridging between strands through Ag2 and Ag4. C91A and C92A are part of a third fullerene whose other atoms are omitted for clarity, as are all hydrogen and fluorine atoms.

strand has a direction, as seen in Figure 1, and that these two adjacent strands are running in opposite directions. In this view, some of the ligation about Ag4 has been omitted for clarity.

There is a second mode of interchain connection made through bridging between Ag4 and Ag2. These connections are shown in Figure 3. Three strands of the linear unit shown in Figure 1 are involved in this bridging arrangement, although, for clarity, only two carbon atoms of the fullerene cage in one strand are shown. Within this portion, the Ag2 to Ag4A distance is 3.654(1) Å and the Ag4 to Ag4A distance is 3.838(1) Å. These distances are much longer than the Ag1···Ag3 separation of 3.1652(7) Å, and there are no argentophilic interactions in the portion of the structure shown in Figure 3.

The functionalized fullerene in this polymer retains the basic structures found for $C_{60}(N(CH_2CH_2)_2N)$.[16,17] Attachment of addends to the 6:6 ring junctions of C_{60} generally results in elongation of the C−C bonds that are involved. In a well-determined structure of C_{60}, the C−C distances at a 6:6 ring junction fall in the range of 1.379(3)−1.396(3)Å, whereas those at 5:6 ring junctions fall in the 1.440(3)−1.461(3) Å range.[18] However, in $C_{60}(N(CH_2CH_2)_2N)$, the C−C distance at the 6:6 ring junction where the amine addition has occurred is elongated to 1.624(8) Å. In $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$, the corresponding C−C distances are similar, 1.604(6) Å for C1−C2 and 1.627(6) Å for C61−C62. On the other hand, the coordination of the Ag(I) ions to the carbon atoms of $C_{60}(N(CH_2CH_2)_2N)$ does not produce a major elongation of the attached C−C bond. For the two carbon atoms attached to Ag1, the C13−C30 bond length is 1.416(6) Å, whereas, for the two carbon atoms attached to Ag2, the C91−C92 distance is 1.403(7) Å. For comparison, attachment of $Pt^0(PPh_3)_2$ or $Ir^I(CO)Cl(PPh_3)_2$ units to C_{60} produces a more significant elongation of the C−C bond at the point of attachment. Thus, for $(\eta^2\text{-}C_{60})Pt^0(PPh_3)_2$, the C−C bond distance between the two carbon atoms bonded to platinum is 1.50(3) Å,[19] and, for $(\eta^2\text{-}C_{60})Ir^I(CO)Cl(PPh_3)_2$, the corresponding C−C distance is 1.53(3) Å.[20]

In regard to the structure of the fullerene portion of this polymer, we have also examined the pyramidalization angles of the carbon atoms in the fullerene.[21] (The pyramidalization angle, θ_p, is 0° for graphite; for C_{60}, it is 11.6°). As expected,

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Figure 4. Drawing of $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$ with 50% thermal contours. For clarity, the positions of hydrogen atoms are not shown and the solvate molecules are omitted.

the four-coordinate carbon atoms attached to nitrogen atoms are highly pyramidalized with $\theta_p = 19.6°$ for C1, 19.2° for C2, 19.3° for C61, and 19.5° for C62. However, for the four carbon atoms coordinated to Ag(I) ions, the pyramidalization angles (11.5° for C12, 12.7° for C30, 12.4° for C91, and 12.1° for C92) are similar to the θ_p in C_{60}.

Structural Results for $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$. Crystals of this complex were obtained through the slow evaporation of a layered combination of a dichloromethane solution of $C_{60}(N(CH_2CH_2)_2N)$ and a methanol solution of silver nitrate. The thin, brown plates start to form within a few weeks. Crystallographic data are contained in Table 1.

As shown in Figure 4, $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)$ is a simple, but rather large, coordination complex with two $C_{60}(N(CH_2CH_2)_2N)$ ligands and a nitrate ion coordinated to Ag(I). The Ag−N distances are similar, Ag1−N3, 2.249(5) Å and Ag1−N4, 2.252(5) Å, whereas the Ag1−O1 distance (2.494(5) Å) is longer. The N3−Ag1−N4 angle is quite open, 159.72(17)°, whereas the N(3)−Ag(1)−O(1) and N(4)−Ag(1)−O(1) angles, 97.95(17) and 100.44(16)°, respectively, are narrower. The wide N3−Ag1−N4 angle allows the bulky fullerene moieties to be positioned appropriately far apart. Despite this wide angle, the sum of the N−Ag−N angle and the two N−Ag−O angles is 358.11°, and, consequently, Ag1 has planar, approximately T-shaped coordination. The shortest distance between individual cage carbon atoms in the two coordinated C_{60}-$(N(CH_2CH_2)_2N)$ molecules is 4.022(7) Å.

This bisfullerene complex packs in clearly defined columns, as seen in Figure 5, so that the fullerene cages face each other. The silver nitrate portions are aligned in a similar region, but unlike the other two compounds reported here, there is no bridging by the anions to form any sort of a polymeric unit. The solvate molecules also do not exhibit any unusual contacts with the complex.

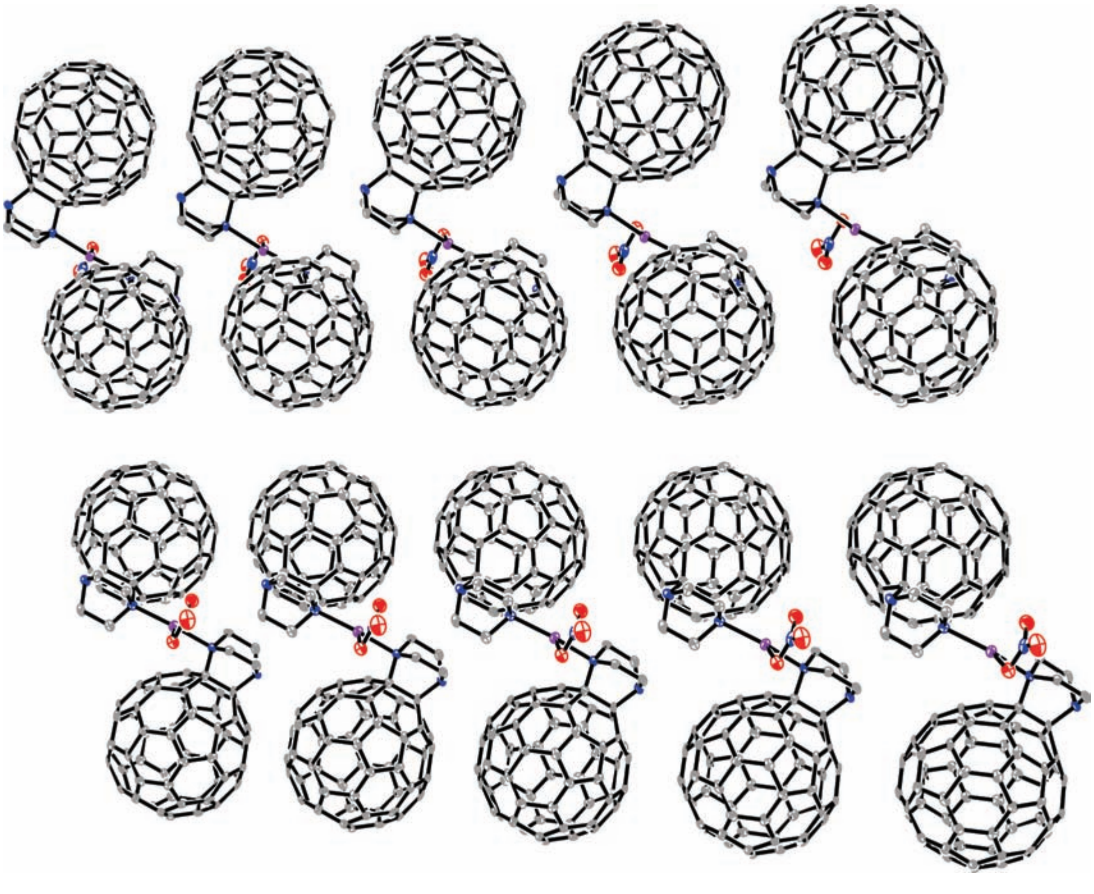

Figure 5. Drawing of $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$ showing the interactions between molecules. For clarity, the positions of hydrogen atoms and the solvate molecules are not shown.

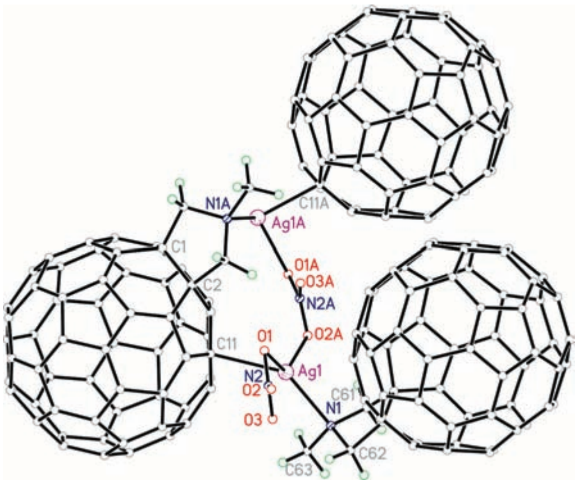

Figure 6. Drawing of $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\} \cdot 0.25CH_3OH$ showing the first polymeric chain. For clarity, the atoms are shown as arbitrarily sized circles.

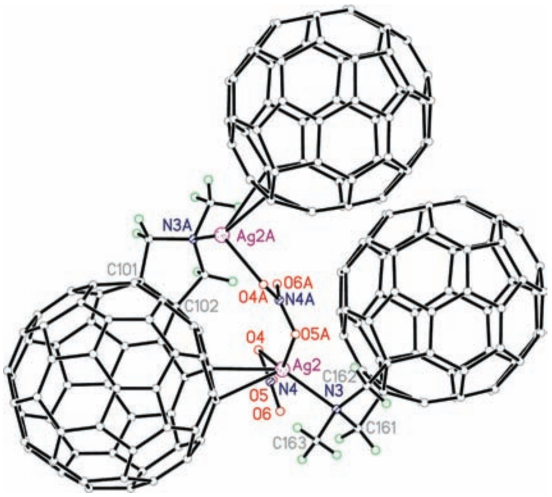

Figure 7. Drawing of $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\} \cdot 0.25CH_3OH$ showing the second polymeric chain. For clarity, the atoms are shown as arbitrarily sized circles.

Structural Results for $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\} \cdot 0.25CH_3OH$. Crystals of this organosilver polymer were obtained through the slow evaporation of a layered combination of a saturated toluene solution of *N*-methyl-3,4-fullero[60]pyrrolidine and a saturated methanol solution of silver nitrate. The red plates start to form within a few weeks. Crystallographic data are provided in Table 1.

In $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\} \cdot 0.25CH_3OH$, there are two Ag(I) ions, two nitrate ions, two molecules of *N*-methyl-3,4-fullero[60]pyrrolidine, and one-half of an uncoordinated methanol molecule in the asymmetric unit. Two polymeric strands are formed by the *N*-methyl-3,4-fullero[60]pyrrolidine molecules and the silver nitrate. A portion of one of the polymeric strands is shown in Figure 6. Ag1 is coordinated to the carbon cage of one functionalized fullerene in η^1-fashion and to the tertiary nitrogen of a neighboring *N*-methyl-3,4-fullero[60]pyrrolidine molecule. The Ag1−C11 distance is 2.518(15) Å, whereas the Ag1−N1 bond length is 2.346(12) Å. Each Ag(I) ion is also bonded to the oxygen atoms of two nitrate ions. The Ag1−O1 distance is 2.464(10) Å, whereas the Ag1−O2A distance is 2.570(11) Å. Consequently, each Ag(I) ion has a distorted, tetrahedral geometry with a wide array of angles between the ligating atoms: C11−Ag1−N1, 137.3(5)°; N1−Ag1−O1, 130.6(4)°; O1−Ag1−O2A, 136.6(4)°; and O2A−Ag1−C11, 94.2(4)°.

A portion of the second strand, which has a structure similar to the first strand, is shown in Figure 7. The major difference involves the nature of the interaction of the Ag(I) ion with the fullerene carbon atoms. Whereas, in the first strand, there is η^1-coordination of the Ag(I) ion to a cage carbon atom, in the second strand, the Ag(I) ion coordinates the adjacent carbon cage in a distorted η^2-fashion, with a short Ag2−C112 distance of 2.473(16) Å and a long Ag2−C113 distance of 2.697(15) Å. Such distortions are common with η^2-coordination of Ag(I).[22] Other relevant bond distances are Ag2−N3, 2.347(12) Å and Ag2−O4, 2.514(10) Å.

The four-coordinate carbon atoms attached to the pyrrolidine function are highly pyramidalized, with $\theta_p = 19.6°$ for C1, 19.2° for C2, 18.2° for C101, and 20.1° for C102. However, for the carbon atom coordinated to the Ag1, the pyramidalization angle (10.5°) is less than that in C_{60} (11.6°). For the carbon atoms bonded to Ag2, the corresponding pyramidalization angles are 10.7° for C121 and 11.0° for C122.

Like the other Ag(I) complexes, this organosilver polymer packs in clearly defined columns so that the fullerene cages face each other, as seen in Figure 8. The nitrate ions and the silver ions are aligned in columns, as noted in the previous two structures.

Conclusions

Three new Ag(I) complexes with fullerene-containing ligands have been prepared and their crystal structures determined. All three have well-ordered fullerene cages, and, consequently, the details of the Ag(I) ion interactions with the fullerenes have been determined to a better extent than was possible in $C_{60}\{Ag(NO_3)\}_5$, where the fullerene cage showed orientational disorder. Coordination of Ag(I) to the fullerene carbon atoms in η^2-fashion produces much smaller changes in the cage geometry than does analogous η^2-attachment of $Pt^0(PPh_3)_2$ or $Ir^I(CO)Cl(PPh_3)_2$ groups. Similarly, coordination of Ag(I) to the fullerene carbon atoms in η^1-fashion does not perturb the pyramidalization of the cage carbon atom. The anions play a significant role in the structures of the Ag(I) complexes of C_{60} or C_{60}-containing molecules and serve as bridges between the individual Ag(I) ions in all cases, except the simple monomer $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3) \cdot 0.5CH_3OH \cdot CH_2Cl_2$.

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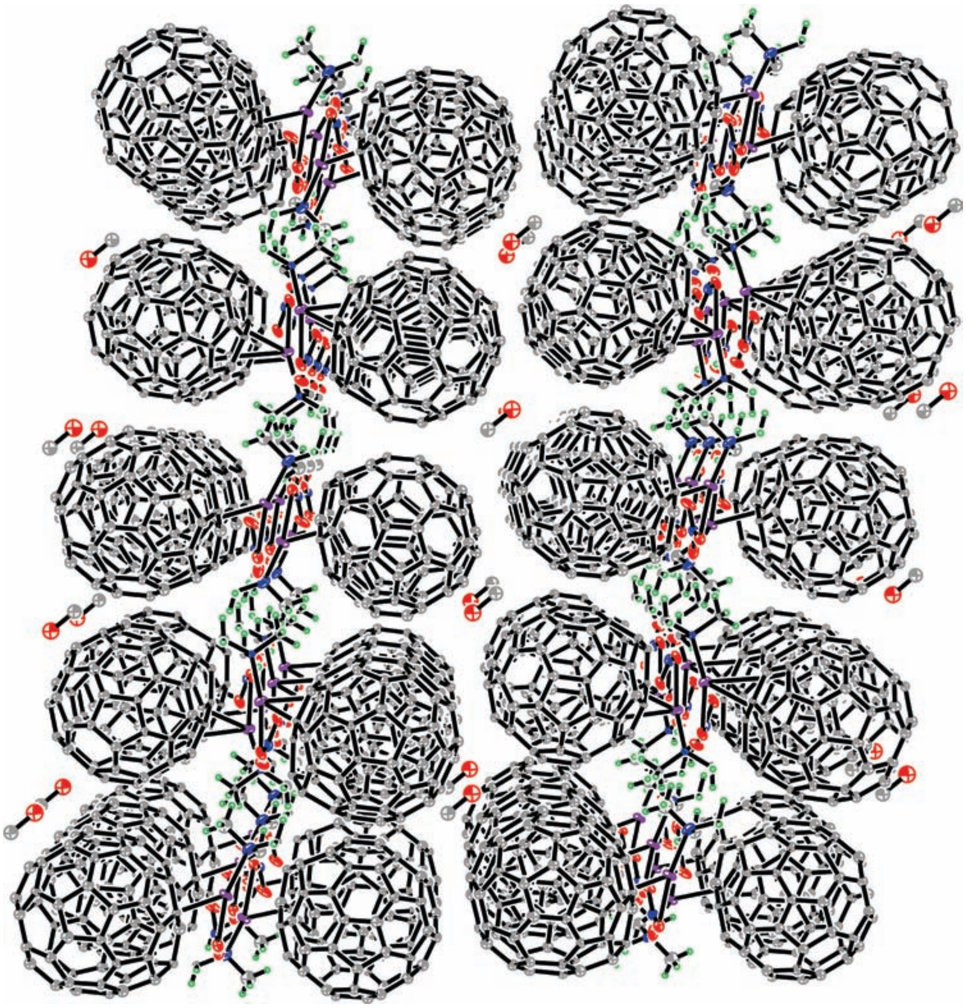

Figure 8. Drawing of $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\}\cdot 0.25CH_3OH$ showing the interactions between molecules and the location of the methanol molecules.

Experimental Section

Preparation of Compounds. Samples of $C_{60}(N(CH_2CH_2)_2N)$[16,23,24] and $C_{60}(CH_2N(CH_3)CH_2)$[25] were prepared as described previously.

$\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$. A saturated carbon disulfide solution of 5.0 mg (0.0060 mmol) of $C_{60}(N(CH_2CH_2)_2N)$ was filtered and transferred into a 200 mm × 6 mm i.d. glass tube. A filtered, saturated carbon disulfide solution of 0.6 mg (0.0029 mmol) of Ag(I) trifluoroacetate was added over the carbon disulfide solution of $C_{60}(N(CH_2CH_2)_2N)$. The two solutions did not form layers, regardless of the order in which they were added. Consequently, the colorless Ag(I) trifluoroacetate solution and the dark brown solution of $C_{60}(N(CH_2CH_2)_2N)]$ mixed to form a tan-colored solution. Red-brown plates formed in this solution within 1 week. The final yield was 1.1 mg (61%). The samples lost crystallinity rapidly upon loss of solvent.

$[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$. A saturated dichloromethane solution of 0.37 mg (0.00046 mmol) of $C_{60}(N(CH_2CH_2)_2N)$ was filtered into a 200 mm × 6 mm i.d. glass tube. A filtered, saturated methanol solution of 9.0 mg (0.053 mmol) of silver nitrate was carefully layered on top. The two solutions formed distinct layers. Brown plates formed within a few weeks in the dichloromethane layer. The crystals decomposed rapidly upon loss of solvent.

$\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\}\cdot 0.25CH_3OH$. A saturated toluene solution of 1.2 mg (0.0015 mmol) of *N*-methyl-3,4-fullero[60]pyrrolidine was filtered and transferred into a 200 mm × 6 mm i.d. glass tube. A filtered, saturated methanol solution of 9.0 mg (0.053 mmol) of silver nitrate was slowly poured over the toluene solution. The two solutions formed distinct layers. Red plates formed within a few weeks in the toluene layer. The final yield was 0.027 mg (20%).

X-ray Data Collection. The crystals were carefully loosened from the sides of the glass tubes in which they were grown and immediately dumped into mother-liquor-saturated Paratone oil on a microscope slide. The loss of crystallinity of the crystal through solvent evaporation was problematic, particularly for the crystals incorporating carbon disulfide molecules. Those crystals significantly deteriorated during sample selection under the microscope. To avoid loss of carbon disulfide, the sample-bearing microscope slide was cooled by placing it over dry ice. Suitable crystals of each compound were mounted onto glass fibers and placed in the 90 K dinitrogen cold stream of a Bruker SMART APEX II or Brucker SMART 1000 diffractometer with Mo Kα radiation. Crystallographic data are reported in Table 1.

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Solution and Structure Refinements. Calculations for the structures were performed using SHELXS-97 and SHELXL-97.[26] Tables of neutral atom scattering factors, *f*′ and *f*″, and absorption coefficients are from a standard source.[27] A semi-empirical absorption correction utilizing equivalents was employed.[28] The structures were all solved via direct methods. All hydrogen atoms were located in difference Fourier maps and included through the use of a riding model.

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Supporting Information Available: Figures SI1−SI3 showing some details of the numbering for the three complexes and Figures SI4 and SI5 showing the pyramidalization angles for the fullerene carbon atoms. X-ray crystallographic files for $\{[C_{60}(N(CH_2CH_2)_2N)][Ag(O_2CCF_3)]_2\}\cdot CS_2$, $[C_{60}(N(CH_2CH_2)_2N)]_2Ag(NO_3)\cdot 0.5CH_3OH\cdot CH_2Cl_2$, and $\{[C_{60}(CH_2N(CH_3)CH_2)]Ag(NO_3)\}\cdot 0.25CH_3OH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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