

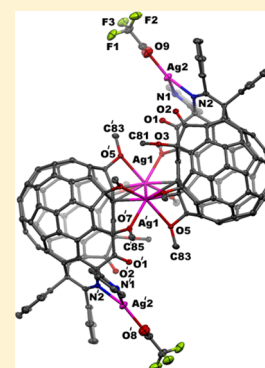
# Silver(I)-Mediated Modification, Dimerization, and Polymerization of an Open-Cage Fullerene

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**S** Supporting Information

**ABSTRACT:** The reactions of the open-cage fullerene, **MMK-9**, with an open 12-membered ring on its surface and silver(I) salts have been examined. The structure of **MMK-9** itself has been determined by single-crystal X-ray diffraction. **MMK-9** reacts with silver trifluoroacetate in air to form the dimer,  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgO}_2\text{CCF}_3)\}_2$ . Remarkably, five MeO groups have added to the surface of the open cage in a pattern that surrounds a pentagon immediately adjacent to the opening in the cage. Dioxxygen has been implicated as the oxidant in this unusual addition of five groups to the open cage. Two silver ions connected to each other by a short argentophilic interaction reside at the core of the centrosymmetric dimer. The reaction of silver nitrate with **MMK-9** yields the crystalline polymer,  $[\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgOCH}_3)\}_2 \cdot \text{H}_2\text{O}]_n$ . This polymer consists of dimeric  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}\}_2$  units that are connected into strands through silver ions, which are chelated by the amine functions of one open cage and bound in  $\eta^2$ -fashion to a pair of carbon atoms on an adjacent open cage.



## INTRODUCTION

The curved outer surface of fullerenes with its array of pentagons and hexagons has attracted attention ever since the initial discovery of  $\text{C}_{60}$ .<sup>1</sup> Once  $\text{C}_{60}$  was isolated as a solid,<sup>2</sup> the reactivity of its outer surface was explored, and various adducts have been found to be useful in areas extending from solar energy collection and storage to medical applications.<sup>3–5</sup> The closed interior space of this highly symmetrical molecule has also fascinated chemists. Indeed, almost immediately after  $\text{C}_{60}$  was discovered, and before it was available in solid form, endohedral fullerenes with lanthanum ions on the inside such as  $\text{La}@\text{C}_{60}$  and  $\text{La}_2\text{C}_{60}$  were detected in gas-phase studies.<sup>6</sup> Endohedral metallofullerenes have also been obtained in soluble solid form<sup>7</sup> and have been considered for use as magnetic resonance contrast agents and in nuclear medical applications.<sup>8–10</sup> When  $\text{C}_{60}$  is prepared using the usual electrical arc method in a low-pressure helium atmosphere, small amounts of the endohedral  $\text{He}@\text{C}_{60}$  are also produced.<sup>11</sup>

By opening a hole in a fullerene cage, it is possible to allow chemical access to the interior of the molecule. A number of such open-cage fullerenes have been synthesized. The first open-cage fullerene with one  $\sigma$ -bond removed was synthesized in a reaction between  $\text{C}_{60}$  and diazomethane by Wudl and his co-workers in 1992.<sup>12</sup> Later, in 1995, Wudl and Prato reported that MEM-substituted ketolactam derivatives of  $\text{C}_{60}$  underwent photo-oxygenation of the cage to produce a 10-membered ring opening in the cage.<sup>13</sup> Subsequently, there have also been reports on manipulating the size of the opening, starting with smaller openings and expanding the orifice size to 12-, 13-, 15-, and even 19-membered ring openings.<sup>14</sup> In a tour de force of synthetic chemistry, holes have been opened in  $\text{C}_{60}$ , dihydrogen, or water inserted into the open cage under

pressure, and then the opening has been repaired to form macroscopic quantities of  $\text{H}_2@\text{C}_{60}$  and  $\text{H}_2\text{O}@\text{C}_{60}$ .<sup>15,16</sup>

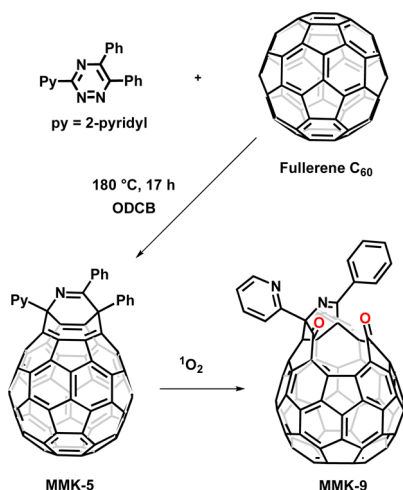
Open-cage fullerenes also have the potential to bind metal ions and to serve as precursors for the chemical synthesis of new endohedral metallofullerenes. Many of the orifices in open-cage fullerenes are lined with Lewis base functionalities that should facilitate coordination of various metal ions. Although open-cage fullerenes have been considered as potential ligands,<sup>17–19</sup> little work in this area has actually been accomplished. In 1996, Rubin and co-workers reported the first example of an adduct formed by insertion of a cobalt atom into one pentagon ring of the open-cage bisfulleroid  $\text{C}_{64}\text{H}_4$ .<sup>20</sup> In that report, a C–C bond on the rim goes through an oxidative addition and ruptures to facilitate orifice expansion and carbon coordination to cobalt and results in the formation of  $\text{CpCo}(\eta^4\text{-C}_{64}\text{H}_4)$ . Triosmium carbonyl clusters show a similar chemistry by oxidative insertion of one of the osmium atoms into a five-membered ring of fullerene, leading to an annulene architecture.<sup>21</sup> Despite great potentials of open-cage fullerenes, so far there are no reports on supramolecular structures (dimers or polymers) of these molecules with metals.

Here, we examine the reactions of silver ions with the open-cage fullerene **MMK-9**.<sup>22</sup> (We use the authors' initials followed by the number used in ref 22 to designate the compounds used here.) **MMK-9** has been prepared by the route shown in Scheme 1. The structure of the precursor **MMK-5** was determined through spectroscopic and crystallographic studies, while **MMK-9** was examined only by spectroscopic means. The formation of **MMK-9** was accompanied by the production of two other compounds, one an isomer of **MMK-9**, but **MMK-9**

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Scheme 1. Formation of the Open-Cage MMK-9



was the major product. Previous studies of this molecule have monitored the incorporation of an H<sub>2</sub>/HD mixture into MMK-9 by <sup>1</sup>H NMR spectroscopy<sup>23</sup> and have examined its reaction with Ru<sub>3</sub>(CO)<sub>12</sub>.<sup>24,25</sup> The reaction with Ru<sub>3</sub>(CO)<sub>12</sub> is complex and involves coordination of ruthenium atoms to the oxygen atoms of MMK-9 as well as the formation of a C–C bond between the adjacent carbon atoms to reduce the size of the orifice. Additionally, reactions that lead to the expansion of the opening in MMK-9 have been examined.<sup>26,27</sup> In this report, we structurally characterize MMK-9 as well as two open-cage adducts with silver salts.

## RESULTS AND DISCUSSION

**Structural Characterization of the Open-Cage Adduct, MMK-9.** A sample of MMK-9 was prepared as shown in Scheme 1 by a previously described method.<sup>21</sup> Brown plates of MMK-9·2.5(C<sub>6</sub>H<sub>6</sub>) were obtained by slow evaporation of a benzene solution of the compound. The structure of MMK-9 as determined by single-crystal X-ray diffraction is shown in Figure 1. There is a 12-membered ring that surrounds the

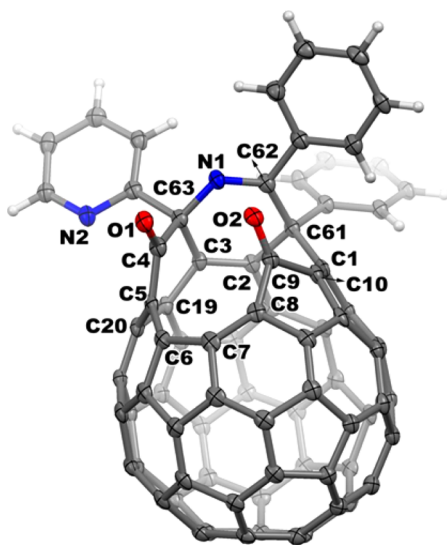


Figure 1. Structure of the oxygenated open-cage fullerene MMK-9 with thermal ellipsoids at 50% probability. The solvent molecules are omitted for clarity.

opening in the formed fullerene cage. The O1–C4 and O2–C9 bond distances (1.214(4) and 1.201(4) Å, respectively) are indicative of the presence of keto groups. The bond that once existed in MMK-5 between C4 and C9 has broken, and the resulting nonbonded C4···C9 distance is 3.130(5) Å in MMK-9. Despite the size of the orifice with 12 atoms on the rim, the space-filling diagrams in Figure 2 show little access to the interior space of the cage.

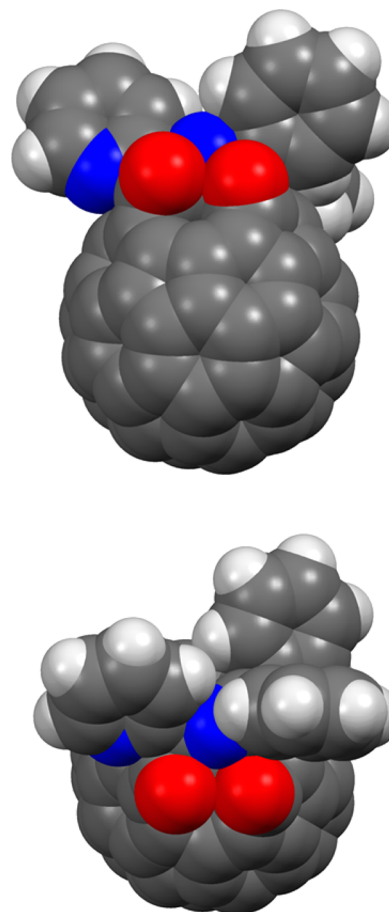


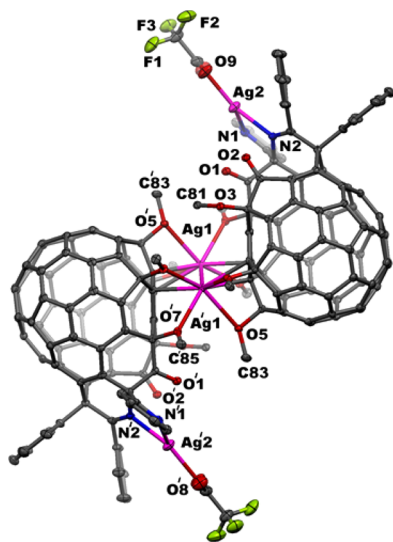
Figure 2. Two space-filling views of MMK-9 looking down the orifice. Color codes: carbon, gray; nitrogen, blue; oxygen, red; and hydrogen, white. Solvent molecules are not shown for clarity.

Individual molecules of MMK-9 are chiral. However, MMK-9·2.5(C<sub>6</sub>H<sub>6</sub>) crystallizes in a centrosymmetric space group. Consequently, an individual crystal contains a racemate.

**Formation and Structure of the Dimer, {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>}**. When a solution of silver trifluoroacetate in methanol was layered over a solution of MMK-9 in dichloromethane, black crystals of {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>·4CH<sub>2</sub>Cl<sub>2</sub>} formed at the interface of the solutions. These black crystals are insoluble in common organic solvents or water. The structure of the product has been determined by single-crystal X-ray diffraction. The asymmetric unit contains one molecule of MMK-9 with five MeO groups attached to it, two Ag<sup>+</sup> cations, and one trifluoroacetate anion. The dimer is formed by inversion of this unit through a crystallographic center of symmetry. In the asymmetric unit, there are also one fully ordered and fully occupied dichloromethane molecule, another dichloromethane molecule that is ordered but has a half occupancy, and a dichloromethane

molecule with half an occupancy, which is disordered over two positions (25%:25%).

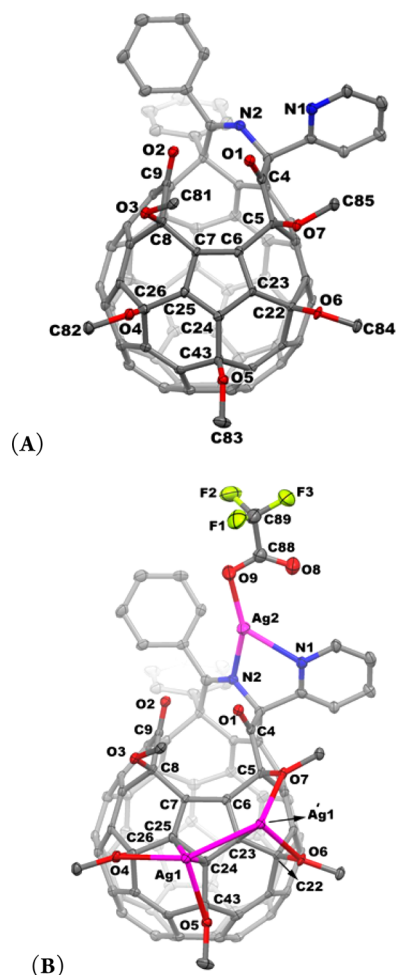
The structure of the entire centrosymmetric dimer is shown in Figure 3. There are several interesting features in this



**Figure 3.** Structure of the dimer  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgO}_2\text{CCF}_3)\}_2$ . Thermal contours are drawn at the 50% probability level.

structure. At the center there are two silver ions (Ag1 and its symmetry generated counterpart Ag1') in close proximity. The Ag1–Ag1' distance is 2.8368(12) Å. This distance is indicative of an argentophilic interaction between the two ions and is at the short end of Ag–Ag distances for such interactions (Table 1).<sup>28</sup>

In an unanticipated reaction, five MeO groups have been added to the cage to surround an isolated pentagon (C6–C7–C23–C24–C25) as shown more clearly in Figure 4 and in Scheme 2. Ag1 is coordinated to this pentagon through  $\eta^2$ -coordination, with nearly similar Ag–C distances of Ag1–C24, 2.383(8) Å, and Ag1–C23, 2.462(8) Å. This silver atom is also coordinated to four of the MeO groups: two in the asymmetric unit and two in the neighboring cage. Relevant



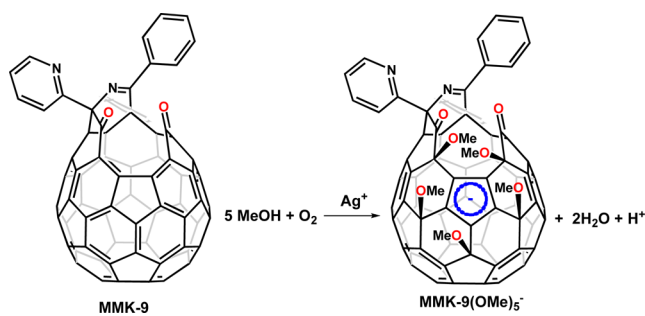
**Figure 4.** (A) A view of one of the open cages in  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgO}_2\text{CCF}_3)\}_2$  that shows how the five MeO units are distributed around one pentagon. (B) A similar view of the open-cage adduct with the silver ion interactions added. Thermal contours are drawn at the 50% probability.

bond distances are given in Table 1. In addition, Ag1 binds to the neighboring cage through Ag1–C'23 with the bond

**Table 1.** Selected Bond Distances in Dimeric  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgO}_2\text{CCF}_3)\}_2$  and Polymeric  $[\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgOCH}_3)\}_2 \cdot \text{H}_2\text{O}]_n$

distance	dimer <sup>a</sup>	polymer A <sup>b</sup>	distance	polymer B <sup>b</sup>
Ag1...Ag1'	2.8368(12)	2.8628(16)	Ag3...Ag3'	2.8526(18)
Ag1–C24	2.383(8)	2.431(9)	Ag3–C109	2.353(9)
Ag1–C25	2.591(8)	2.582(9)	Ag3–C110	2.585(10)
Ag1–O4	2.718(6)	2.696(7)	Ag3–O11	2.749(9)
Ag1–O5	2.633(6)	2.645(7)	Ag3–O12	2.687(7)
Ag1'–C23	2.462(8)	2.427(10)	Ag3'–C108	2.471(10)
Ag1'–O6	2.460(5)	2.524(7)	Ag3'–O13	2.497(8)
Ag1'–O7	2.501(6)	2.494(6)	Ag3'–O14	2.460(7)
Ag2–N1	2.350(8)	2.326(10)	Ag4–N3	2.373(12)
Ag2–N2	2.295(7)	2.458(8)	Ag4–N4	2.420(9)
Ag2–O9	2.200(8)	2.509(11)		
Ag2–O15A		2.490(19)		
Ag2–C37		2.509(11)	Ag4–C122	2.521(11)
Ag2–C53		2.344(10)	Ag4–C138	2.345(12)

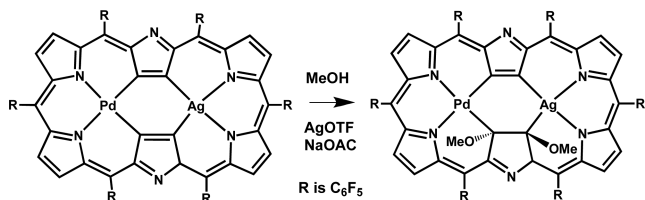
<sup>a</sup>Dimer =  $\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgO}_2\text{CCF}_3)\}_2$ . <sup>b</sup>Polymer =  $[\{\text{MMK-9}(\text{OCH}_3)_5\text{Ag}(\text{AgOCH}_3)\}_2 \cdot \text{H}_2\text{O}]_n$ . Polymer A involves Ag1 and Ag2 as shown in Figure 6, while Polymer B involves Ag3 and Ag4.

**Scheme 2. Silver-Mediated Addition of MeO Groups to MMK-9**

distance of 2.462(8) Å. As shown in Figure 3, the silver–silver bond is fully surrounded and isolated by the 10 MeO groups attached to the dimer.

**Nature of the Silver Ion-Mediated MeO Addition Process.** The addition of five MeO units to MMK-9 involves an oxidative process as seen in Scheme 2. (This scheme is drawn to emphasize the formation of the anion MMK-9(OCH<sub>3</sub>)<sub>5</sub><sup>-</sup>, which coordinates silver ion in the products reported here. The proton generated in Scheme 2 is likely to be taken up by the amine sites in the unreacted MMK-9 present in the reaction medium.) The pattern of MeO addition seen here is similar to the arrangement of addends found by Nakamura and co-workers in the formation of C<sub>60</sub>Ph<sub>5</sub>H through the reaction of PhMgBr and Me<sub>2</sub>SCuBr with C<sub>60</sub> (vide infra).<sup>29,30</sup> Crystals of {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>·4CH<sub>2</sub>Cl<sub>2</sub>} were grown under ambient conditions in the presence of methanol. The same compound is formed when MMK-9 is dissolved in benzene, toluene, or chloroform instead of dichloromethane and layered by silver trifluoroacetate in methanol. No crystals formed when the silver trifluoroacetate solution was prepared in other solvents, including ethanol and 1-propanol. There was no evidence of the formation of metallic silver during the MeO addition. Thus, while silver ion may act as catalyst in this transformation, it is not the ultimate oxidant in the reaction. Significantly, no crystals formed when we performed the identical crystallization process under a dinitrogen atmosphere in the glovebox with dry solvents. This observation implicates dioxygen as the oxidant in the formation of {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>·4CH<sub>2</sub>Cl<sub>2</sub>}.

There is little precedent for the reaction shown in Scheme 2. We could find only one related reaction that involved silver ion. That reaction involved the addition of two MeO units across a double bond in a dimetallo macrocycle as shown in Scheme 3.<sup>31</sup> Additionally, the photochemical reaction of C<sub>60</sub> with methanol in the presence acetyl glycine was reported to form the diadduct,

**Scheme 3. Silver-Mediated Addition of MeO Groups to a Dimetallo macrocycle<sup>a</sup>**<sup>a</sup>See ref 31.

C<sub>60</sub>(OMe)<sub>2</sub>.<sup>32</sup> Alkoxy adducts of C<sub>60</sub> have also been obtained via substitution reactions of C<sub>60</sub>Cl<sub>6</sub>.<sup>33</sup>

We have also examined the possibility that silver(I) salts might promote a similar addition reaction with pristine C<sub>60</sub>. However, we found no evidence of an addition reaction between C<sub>60</sub> in benzene solution with silver trifluoroacetate in methanol. This lack of reactivity may come from a need to have Lewis base sites available to coordinate to the silver ion during the addition process. Note that MMK-9 has two oxygen atoms immediately adjacent to the site of addition, and these two basic sites may be transiently involved in silver ion coordination during the addition process.

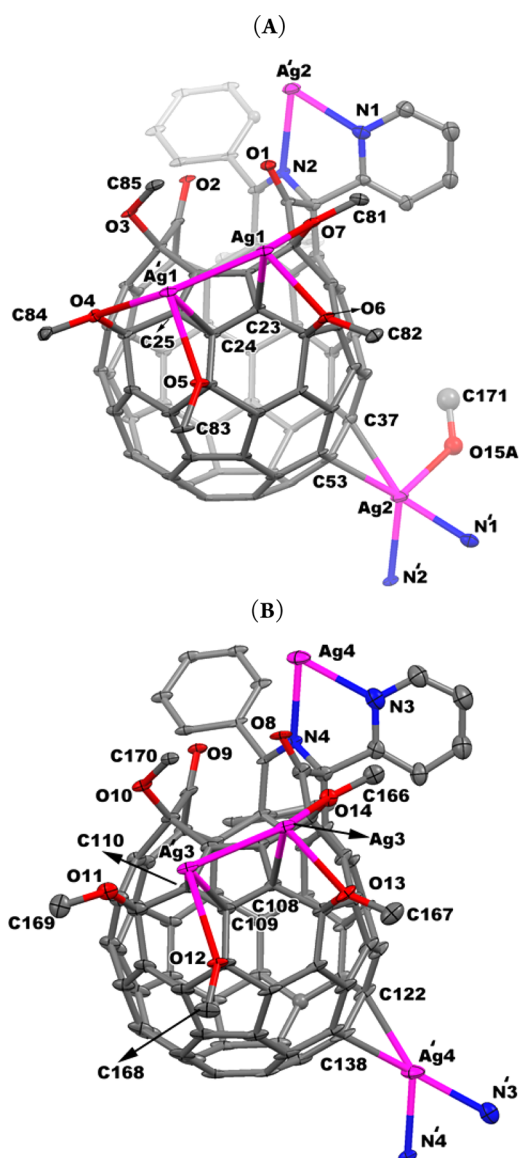
We did find that using different silver counterions altered the nature of the product obtained from the reaction of methanol solutions of silver salts with MMK-9, as documented in the next section.

**Preparation and Structure of the Polymer, {[MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgOCH<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O]}<sub>n</sub>.** When a solution of MMK-9 in dichloromethane was layered with a solution of silver nitrate in methanol, black plates of {[MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgOCH<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O]}<sub>n</sub> formed at the interface of the solutions. These crystals, like those of the dimer, are insoluble in organic solvents. The asymmetric unit for this compound consists of two MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag units, which dimerize in a fashion similar to the situation in dimeric {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>·4CH<sub>2</sub>Cl<sub>2</sub>}. The two independent MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag units and the adjacent silver ions are shown in Figure 5. These two entities are similar to the corresponding portion of the dimer {MMK-9(OCH<sub>3</sub>)<sub>5</sub>Ag(AgO<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>} shown in Figure 4B. In both the dimer and the polymer, five MeO units have been added to the open cage in a similar fashion. In both compounds, two silver ions are nestled near the five-membered ring that is surrounded by five MeO groups.

The major difference in the polymer when compared to the dimer is the bonding about the silver ions (Ag<sub>2</sub> and Ag<sub>4</sub>) that are chelated by two nitrogen atoms. In the dimer, that silver ion (Ag<sub>2</sub>) has trigonal planar coordination with a trifluoroacetate ion providing the third ligand. However, in the polymer, Ag<sub>2</sub> and Ag<sub>4</sub> are coordinated to an adjacent open-cage molecule through asymmetric η<sup>2</sup>-coordination. It is this new η<sup>2</sup>-coordination of silver to the neighboring open cage that allows the polymeric chain to propagate. Additionally, Ag<sub>2</sub> is loosely coordinated by a methoxide ligand, but there is no corresponding methoxide bound to Ag<sub>4</sub>. The corresponding methoxide ion is located further away. Moreover, the methoxide ion bound to Ag<sub>2</sub> is disordered over two sites, but only one of these is shown in Figure 5.

The units shown in Figure 5 dimerize by reflection through a center of symmetry and propagate through the coordination environment of Ag<sub>2</sub> or Ag<sub>4</sub>. Figure 6 shows a view of one polymeric chain formed from the fragment shown in Figure 5A. A second, different chain is obtained by propagation of the unit shown in Figure 5B.

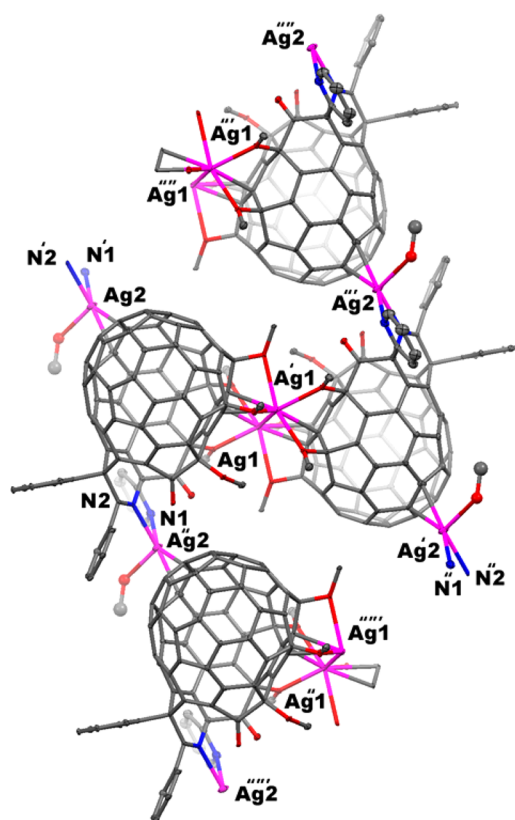
The two chains generated from the fragments in Figure 5 run parallel to each other along the *a* axis of the crystal as shown in Figure 7. Thus, the chains propagate perpendicular to the plane of the page so that only the ends of the chains are seen in Figure 7. As the figure shows, the chains do not pack tightly together. Rather, there is a space consisting of 20.2% of the unit cell that is occupied by poorly defined solvate molecules that have been treated by using the program SQUEEZE.



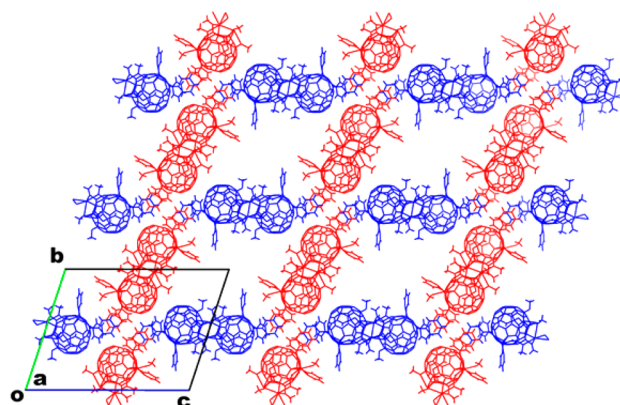
**Figure 5.** Views of the independent MMK-9(OCH<sub>3</sub>)<sub>5</sub> units and the silver ions attached to them in the polymer  $[\{MMK-9(OCH_3)_5Ag(AgOCH_3)_2 \cdot H_2O\}]_n$ . Thermal contours are drawn at the 50% probability.

## CONCLUSIONS

This work demonstrates that silver-mediated reactions of the open-cage fullerene, MMK-9, produce a dimer and a polymer, which are, to our knowledge, the first instances of forming such structures with an open-cage fullerene. Remarkably, the process also involves a facile addition of five MeO units in a pattern that surrounds the pentagon immediately below the cage orifice, as shown in Figure 4A and Scheme 2. This addition pattern is analogous to that observed in organocuprate addition of alkyl or phenyl groups to C<sub>60</sub> or C<sub>70</sub>.<sup>29,30,34</sup> Such addition reactions have produced a number of interesting new fullerene adducts, including buckyferrocene,  $(\eta^5-C_5H_5)Fe(\eta^2-Me_5C_{60})$ .<sup>35</sup> We anticipate that we will be able to utilize the facile addition of MeO units to MMK-9, and hopefully other open-cage fullerenes as well as empty cage fullerenes, to enrich the variety of fullerene compounds available.



**Figure 6.** A drawing of one of the polymeric strands (the one involving Ag1 and Ag2) in  $[\{MMK-9(OCH_3)_5Ag(AgOCH_3)_2 \cdot H_2O\}]_n$ . Thermal contours are drawn at the 50% probability level. A second similar chain is produced from the fragment containing Ag3 and Ag4.



**Figure 7.** A drawing showing the relationship between the two polymeric chains (one colored red involving Ag1 and Ag2, the other colored blue involving Ag3 and Ag4) in  $[\{MMK-9(OCH_3)_5Ag(AgOCH_3)_2 \cdot H_2O\}]_n$ .

## EXPERIMENTAL SECTION

**Synthesis of  $\{(MMK-9)(OCH_3)_5Ag(AgO_2CCF_3)\}_2 \cdot 4CH_2Cl_2$ .** A saturated solution of 1.5 mg (0.0014 mmol) of MMK-9 in 1.2 mL of dichloromethane was added to a 6 mm glass tube and layered with a saturated solution of AgO<sub>2</sub>CCF<sub>3</sub> in methanol. After a few weeks, brown single crystals grew at the interface of the solutions. The yield was 36% based on the recovered starting material.

**Synthesis of the Polymer,  $[\{MMK-9(OCH_3)_5Ag(AgOCH_3)_2 \cdot H_2O\}]_n$ .** A saturated solution of 1.5 mg (0.0014 mmol) of MMK-9 in 1.2 mL of dichloromethane was added to a 6 mm glass tube and layered with a saturated solution of AgNO<sub>3</sub> in methanol. After

standing for a few weeks, brown single crystals of the polymer formed at the interface of the solutions. The yield was 45% based on the recovered starting material.

**Crystal Data for the Open-Cage Fullerene MMK-9.**  $C_{95}H_{29}N_2O_2$ :  $M = 1230.20$  g/mol, brown plates,  $0.309 \times 0.137 \times 0.044$  mm,  $\lambda = 1.54178$  Å (Cu  $K\alpha$ ), monoclinic, space group  $P\bar{1}$  (No. 2),  $a = 10.0211(5)$ ,  $b = 16.2229(9)$ ,  $c = 16.7816(8)$  Å,  $\alpha = 82.685(3)^\circ$ ,  $\beta = 85.938(3)^\circ$ ,  $\gamma = 76.786(3)^\circ$ ,  $V = 2631.9(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 90(2)$  K, 17 249 reflections measured, 8225 unique, which were used in all calculations, Bruker Apex Duo;  $2\theta$  max =  $127.368^\circ$ ; min/max transmission =  $0.5943/0.7536$  (multiscan absorption correction applied); direct and Patterson methods solution; full-matrix least-squares based on  $F^2$  (SHELXT and SHELXL-2014/7).<sup>36,37</sup> The final  $wR(F_2)$  was 0.1781 (all data), conventional  $R_1 = 0.0624$  computed for 8225 reflections with  $I > 2\sigma(I)$  using 923 parameters with 0 restraints.

**Crystal Data for the Dimer  $\{[(MMK-9)(OCH_3)_5Ag(AgO_2CCF_3)]_2 \cdot 4CH_2Cl_2 \cdot C_{89}H_{33.25}Ag_2Cl_4F_3N_2O_9\}$ .**  $M = 1688.96$  g/mol, brown blocks,  $0.196 \times 0.113 \times 0.063$  mm,  $\lambda = 1.54178$  Å (Cu  $K\alpha$ ), monoclinic, space group  $P2_1/c$  (No. 14),  $a = 24.5549(12)$ ,  $b = 13.8358(7)$ ,  $c = 20.0110(9)$  Å,  $\beta = 109.893(2)^\circ$ ,  $V = 6392.8(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 90(2)$  K, 36 485 reflections measured, 11 417 unique, which were used in all calculations, Bruker Apex Duo;  $2\theta$  max =  $136.472^\circ$ ; min/max transmission =  $0.3972/0.6155$  (multiscan absorption correction applied); direct and Patterson methods solution; full-matrix least-squares based on  $F^2$  (SHELXT and SHELXL-2014/7).<sup>36,37</sup> The final  $wR(F_2)$  was 0.2587 (all data), conventional  $R_1 = 0.0964$  computed for 11 417 reflections with  $I > 2\sigma(I)$  using 1012 parameters with 12 restraints.

**Crystal Structure of  $\{[(MMK-9)(OCH_3)_5Ag(AgOCH_3)]_2 \cdot H_2O\}_n$ .**  $C_{172}H_{64}Ag_4N_4O_{17}$ :  $M = 2889.75$  g/mol, brown plate,  $0.187 \times 0.172 \times 0.039$  mm,  $\lambda = 1.54178$  Å (Cu  $K\alpha$ ), triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.5733(4)$ ,  $b = 22.8941(8)$ ,  $c = 29.5418(9)$  Å,  $\alpha = 71.278(2)^\circ$ ,  $\beta = 82.596(2)^\circ$ ,  $\gamma = 83.746(2)^\circ$ ,  $T = 90(2)$  K,  $V = 7332.4(4)$  Å<sup>3</sup>,  $Z = 2$ , 32 617 reflections measured,  $2\theta_{max} = 144.398^\circ$ ; min/max transmission =  $0.5050/0.7533$  (multiscan absorption correction applied); direct and Patterson methods solution; full-matrix least-squares based on  $F^2$  (SHELXT and SHELXL-2014/7).<sup>36,37</sup> Refined as a two-component twin; PLATON/SQUEEZE was used for solvent accessible voids.<sup>38</sup> The final  $wR(F_2)$  was 0.2466 (all data), conventional  $R_1 = 0.0913$  computed for 25 438 reflections with  $I > 2\sigma(I)$  using 1766 parameters with 1614 restraints.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b10394](https://doi.org/10.1021/jacs.6b10394).

Spectroscopic data (PDF)

X-ray crystallographic data for MMK-9 (CIF)

X-ray crystallographic data for  $\{[(MMK-9)(OCH_3)_5Ag(AgO_2CCF_3)]_2 \cdot 4CH_2Cl_2\}$  (CIF)

X-ray crystallographic data for  $\{[(MMK-9)(OCH_3)_5Ag(AgOCH_3)]_2 \cdot H_2O\}_n$  (CIF)

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### Notes

The authors declare no competing financial interest.

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