Formation of a Curved Silver Nitrate Network That Conforms to the Shape of C_{60} and Encapsulates the Fullerene—Structural Characterization of $C_{60}\{Ag(NO_3)\}_5$**

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Dedicated to Professor Raymond M. Keefer on the occasion of his 85th birthday

The nearly spherical architecture of C_{60} makes it an attractive candidate for the construction of larger, supramolecular structures. Containing its curved external surface presents an interesting challenge, since many of the building blocks that are available to the chemist present flat surfaces which need to be manipulated in some fashion in order to effectively surround the fullerene, either in part or entirely. Weak complexes are formed between C_{60} and a number of bowl-shaped molecules including calixarenes,[1] cyclodextrins,[2] and cyclotriveratrylene,[3] and several of these assemblies have been structurally characterized. Metal complexes have been prepared with specific ligands designed to wrap flat benzene rings into curved arms that can encircle C_{60}.[4] Fullerenes are also known to cocrystallize with a variety of molecules that include organic, organometallic, and inorganic species.[5]

Here we report on the creation of a complex network from very simple components, silver(I) nitrate and C_{60}. Although silver ions are known to interact with olefins and arenes, there have been only limited reports of $Ag^+ - C_{60}$ interactions. Mass spectrometric studies have presented evidence for the existence of $[Ag_xC_{60}]^+$ $(x = 1-5)$ and $[Ag(C_{60})_2]^+$ in the gas phase.[6] In solution the electronic spectrum of C_{60} itself is unaffected by the presence of silver ions.[7] However, fullerenes that are chemically modified by the addition of potentially coordinating amino ether groups do show spectroscopic changes that were attributed to $Ag^+ - C_{60}$ π interactions.[8]

Dark red, nearly black blocks of $C_{60}\{Ag(NO_3)\}_5$ were obtained in 63% yield by the diffusion of a solution of silver nitrate in ethanol into a solution of C_{60} in benzene. The structure of the new solid has been determined through a single-crystal X-ray diffraction study. As seen in Figure 1, the solid has a complex structure in which the silver nitrate portion forms a zeolite-like network.[9] Within this network, rounded cavities are formed, and these are occupied by the fullerene molecules. Figure 1a shows a view of the entire structure with van der Waals surfaces; Figure 1b shows the same portion but with the fullerene molecules removed. The cavities that the fullerenes occupy are clearly visible and form apparent channels within the silver nitrate network. However, the silver nitrate network encapsulates each fullerene in a fashion that precludes movement of the fullerene molecules from one cavity to another.

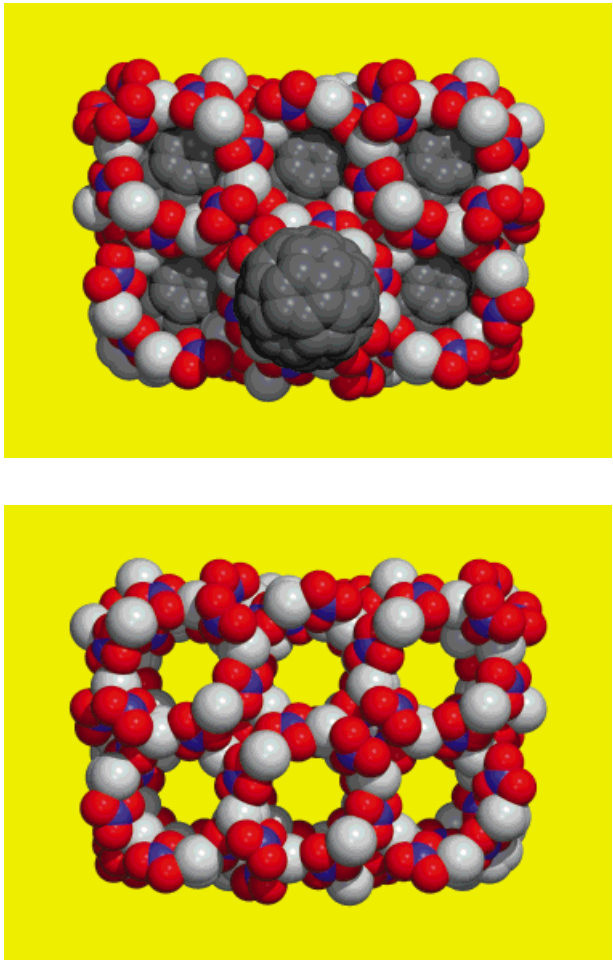

Figure 1. Structure of $C_{60}\{Ag(NO_3)\}_5$ with van der Waals contours for the various atoms. a) A portion of the complete structure with only one fullerene shown in the upper most layer. b) Part of the silver nitrate network with the fullerenes removed. Silver is shown as light gray, oxygen red, nitrogen dark blue, and carbon dark gray.

The nature of the network of silver nitrate ions is shown in Figure 2. There are four "straps" which surround the fullerene in two perpendicular planes. Figure 3 presents some details of the arrangement of one of the straps, the one that comes closest to the fullerene. The nitrate ions have the expected trigonal-planar geometry and are fully ordered. Each silver ion is surrounded by six oxygen atoms with Ag–O distances that range from 2.34(12) to 2.814(12) Å. One of the silver ions, Ag1, resides on a mirror plane perpendicular to *a* (position *m*). A second silver ion, Ag2, also resides on this plane, but is disordered with respect to the mirror plane that is perpendicular to *b* (position *d*). The Ag2···Ag2′ distance is 1.137(9) Å. The third silver ion, Ag3, is disordered with respect to a center of inversion (position *e*) and is separated from its centrosymmetric counterpart by 0.633(13) Å. The molecule of C_{60} falls on a site (position *d*) with *mm* symmetry. In the asymmetric unit there is a total of 1.25 Ag^+, 1.25 $(NO_3)^-$, and 0.25 C_{60}.

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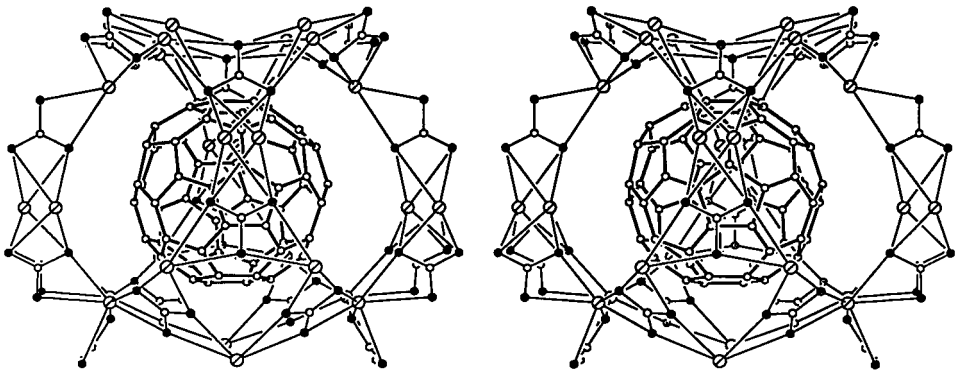

Figure 2. A stereoscopic drawing that shows how the silver nitrate network encapsulates the fullerene. Within the silver nitrate network, the silver ions are indicated by circles with a slash, the nitrogen atoms by circles with a dot in the center, and the oxygen atoms by simple circles.

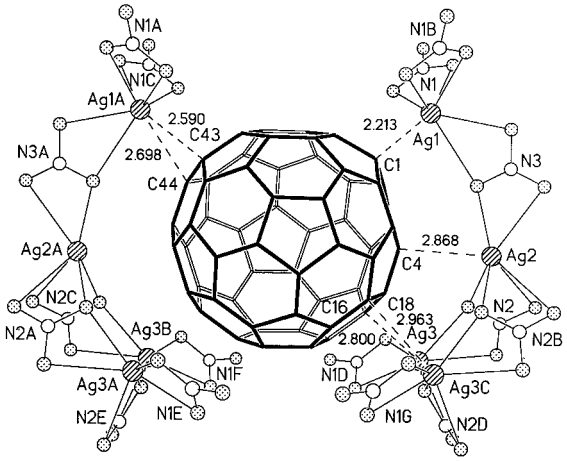

Figure 3. A drawing of a fragment of the structure of $C_{60}\{Ag(NO_3)\}_5$ that shows the interaction of the two closest straps with one orientation of the fullerene. The other orientations of the fullerene involve identical distances.

The fullerene cavity resides at the intersection of two perpendicular mirror planes, but the fullerene molecules themselves are not centered within this site. Rather, the center of the fullerene molecule is shifted by 0.185 Å from the special position of *mm* symmetry, and one of the fullerene mirror planes is rotated by 5.2° from the crystallographic mirror plane. Thus, there are four possible locations for the fullerene within the cavity. Figure 3 shows one of those orientations and the nature of the fullerene–silver contacts along the straps that interact most closely with the fullerene. The other two straps are positioned further away from the fullerene in the cavity shown. The contacts between Ag2 and Ag3 and the fullerene carbon atoms are quite long and do not correspond to normal bonding distances. However, Ag1 does interact with the fullerene in two ways. On one side it engages in η^2 coordination, with Ag–C distances (2.590(10) and 2.698(10) Å) that are within the range found for such bonding.[10] On the opposite side, the Ag1–C1 distance (2.213(6) Å) is quite short, and the location of the silver ion is directly over a single carbon atom so that η^1 coordination is involved. This is the first case of η^1 coordination of a transition metal to a fullerene that is crystallographically determined.[11] It is well established that a silver ion can interact with olefins and aromatic hydrocarbons in both η^1 and η^2 fashion, and that for η^2 bonding the silver ion is not necessarily symmetrically disposed with respect to the olefin.[12]

Despite the good solubility of silver nitrate in water, crystalline $C_{60}\{Ag(NO_3)\}_5$ is stable in the presence of air and moisture. A crystal that was immersed in water for one hour retained its ability to diffract X-rays, but after immersion for 20 hours the crystal, which retained its external shape, no longer gave clear spots on rotation photographs. Crystals of $C_{60}\{Ag(NO_3)\}_5$ are more stable toward exposure to an aqueous solution of sodium chloride. After 28 hours of immersion in a sodium chloride solution, a crystal retained its ability to diffract X-rays, although after five days of immersion it no longer diffracted. The greater stability toward a sodium chloride solution is attributed to precipitation of silver chloride on the crystal surface and the resultant inhibition of diffusion.

Considerable attention has also been given to the intercalation of metal atoms into the C_{60} lattice, where the cubic close packing of the C_{60} molecules creates tetrahedral and octahedral holes.[13] In part work in this area has been prompted by the observation of superconductivity of materials with the composition $(\text{alkali metal})_3C_{60}$.[14] The present study demonstrates that it is possible to use solution-phase techniques to construct new fullerene phases that incorporate inorganic components. It is noteworthy that in $C_{60}\{Ag(NO_3)\}_5$, the cubic close packing of C_{60} molecules is not present. Moreover, $C_{60}\{Ag(NO_3)\}_5$ is the first case in which a fullerene and an ionic component, rather that a second molecular component, cocrystallize. The complex structure found for $C_{60}\{Ag(NO_3)\}_5$ is also related to those of a variety of new solids that have been created from inorganic and organic components.[15] For example, at the opposite end of the size scale, acetylenediide has been fully encapsulated by nine silver ions in $Ag_2C_2 \cdot 8\,AgF$.[16] Additionally, a hydrothermal synthesis of a dense, crystalline inorganic/organic layered compound has been devised to form the fumaric acid complex $[Cu_2(O_2CCH{=}CHCO_2)]$.[17]

Experimental Section

A saturated solution of silver(I) nitrate in absolute ethanol was carefully placed over a solution of C_{60} (2.1 mg, 2.9×10^{-3} mmol) in benzene. The mixture was allowed to stand undisturbed and protected from light for one week. During that time dark red, nearly black cubic crystals formed in 63 % yield (based on C_{60}). The IR spectrum of $C_{60}\{(Ag(NO_3)\}_5$ in a Nujol mull showed a strong broad shoulder in the region between 1339 and 1311 cm^{-1} for the nitrate group and another peak at 1180 cm^{-1} that is characteristic of C_{60}.

Crystal data for $C_{60}\{Ag(NO_3)\}_5$: black block, $0.04 \times 0.10 \times 0.12$ mm, tetragonal, space group $P4_2/nmc$, $a = b = 13.934(3)$, $c = 18.504(3)$ Å, $V = 3835.2(15)$ Å^3, $\lambda = 0.71073$ Å, $Z = 4$, $\rho_{calcd} = 2.719$ Mg m^{-3}; $\mu(Mo_{K\alpha}) = 2.615$ mm^{-1}; ω scans, $2\Theta_{max} = 50°$; $T = 140$ K; of 2049 reflections collected,

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1852 were independent ($R_{int} = 0.033$) and included in the refinement; Lorentzian polarization and absorption corrections (psi scans) performed; min./max. transmission = 0.74/0.90; solution by direct methods(SHELXS-97); refinement by full-matrix least squares based on F^2 (SHELXL-97); 141 parameters, $R = 0.1486$, $wR = 0.2301$ for all data; $R1 = 0.0843$ computed for 1004 observed data ($> 2\sigma(I)$). The fullerene molecule was refined as a rigid group with the use of parameters from a well-determined structure.[18] Twinning is an unlikely explanation for the disorder because there was no evidence of abnormal peak shapes or spurious reflections between layer lines. The space group determination was completely unambiguous; therefore, there was only one minor violation (0, 0, 11) of the conditions for systematic absences. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102135. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Controlling the Secondary Structure of Nonbiological Oligomers with Solvophobic and Coordination Interactions**

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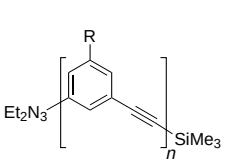
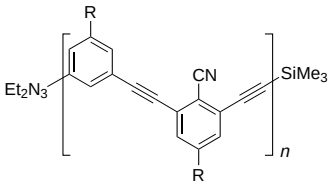
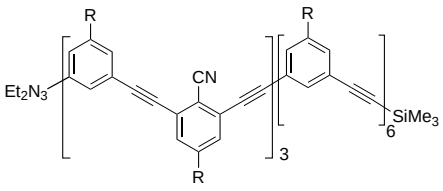
The study of conformationally ordered structures in solution from synthetic chain molecules is an important problem whose ultimate aim is to mimic the properties and functions of natural biopolymers. Well-defined conformations of nonbiological oligomers have been achieved by a variety of strategies including intramolecular hydrogen bonding,[1–3] donor – acceptor complexation,[4] control of monomer torsion through local steric and electrostatic interactions,[1, 5] and metal – ligand interactions.[6–9] Ordered structure in proteins and nucleic acids depends upon a combination of specific and nonspecific noncovalent forces. In general, most evidence supports a picture in which nonspecific hydrophobic interactions provide the energetic driving force for folding, while directional interactions play a structure-defining role. In search of a system that depends on nondirectional forces to drive conformational ordering, we recently reported the solution behavior of a homologous series of *meta*-connected phenylacetylene oligomers **1**.[10] The helical conformation results in a tubular cavity, which upon modification could allow for the creation of novel receptor or catalytic systems.



1, n = 2, 4, 6, 8, 10, 12, 14, 16, 18



2, n = 3
3, n = 6



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R = -$CO_2(CH_2CH_2O)_3CH_3$

We now report one such modification of the tubular cavity that leads to a highly ordered secondary structure controlled

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