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Crystallographic Characterization and Structural Analysis of the First Organic Functionalization Product of the Endohedral Fullerene $Sc_3N@C_{80}$

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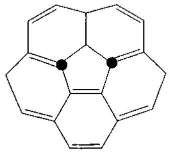
Endohedral fullerenes, fullerenes with atoms in the inside, have been known since fullerene chemistry was in its infancy,[1] and an extensive body of information regarding their spectroscopic properties exists.[2] However, the study of the chemical reactivity of these species has been hampered by the relatively small quantities of endohedrals produced in conventional syntheses. The trimetallic nitride template (TNT) method of fullerene production has afforded macroscopic quantities of the set of three endohedrals, $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{80}$.[3-5] Unlike other known fullerene cages, the I_h C_{80} cage in $Sc_3N@C_{80}$ does not possess any of the reactive pyracylene sites (a 6:6 ring junction abutted by two pentagons). Instead, the I_h C_{80} cage contains only pyrene-type sites (a 6:6 ring junction abutted by a hexagon and a pentagon) and corannulene-type sites (a 6:5 ring junction abutted by two hexagons). Therefore, the I_h C_{80} cage is likely to display unique chemical behavior. Indeed, a previous communication reported that $Sc_3N@C_{80}$ reacts with the diene precursor 6,7-dimethoxyisochroman-3-one to form a Diels−Alder cycloadduct $Sc_3N@C_{80}-C_{10}H_{12}O_2$, (**1**).[6] The NMR data from a ^{13}C-labeled sample suggested that the molecule possesses a plane of symmetry, and three plausible structures were proposed for this adduct. Localized views of the plausible sites of addition are shown as a, b, and c below. Structure b was favored.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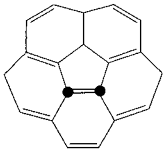
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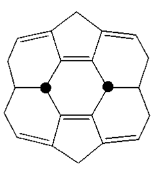
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Here we present a crystallographic characterization of the crystalline $Sc_3N@C_{80}$ cycloadduct, (**1**). It has been shown that a lack of uniformity in the fullerene cage orientations and the high degree of mobility of the encapsulated entities produce varying degrees of disorder in the crystal structures of endohedral fullerenes.[3,5,7,8] However, with the symmetry of the fullerene cage lowered by the added group, **1** crystallizes in a highly ordered fashion which allows detailed structural analysis.

Black crystals of **1**·2 (C_6H_6) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of **1** in benzene and methanol. The results of a structure determination conducted at 91(2) K are seen in Figure 1.[9,10] In the [80]fullerene cage, the 6:5 bonds are slightly longer than the 6:6 bonds. The average of the 6:5 C−C bond distances, excluding those in the vicinity of the addend is 1.437(15) Å, while the average of the 6:6 C−C bond distances is 1.421(18) Å. In contrast in C_{60} the average 6:5 and 6:6 bond distances (1.383(4) and 1.453(5) Å, respectively) differ by a larger amount.[12]

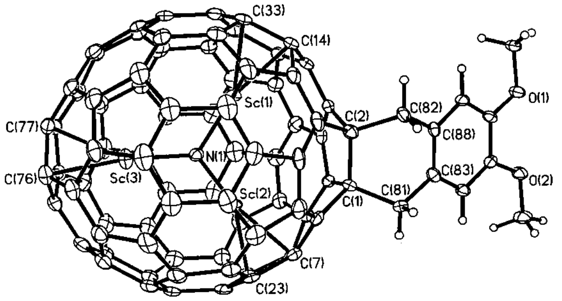

Figure 1. A view of **1** with 50% thermal ellipsoids. Only the main scandium sites and the two shortest Sc−C bonds for each Sc ions are shown. The two benzene molecules are omitted for clarity.

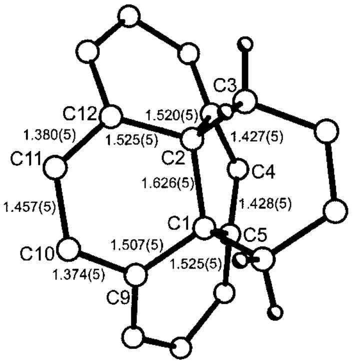

Figure 2. A view of **1** in the vicinity of the addend with the C−C distances in Å amount.[12]

As Figure 1 shows, the cycloaddition occurs in a [4,2] fashion to a C−C bond at a 6:5 ring junction (corannulene-type site), which is consistent with the structure b previously proposed.[6] As seen in Figure 2, the C1−C2 distance, 1.626(5) Å, is substantially elongated when its length is compared to the average C−C distance (1.437(15) Å) at unaltered 6:5 ring junctions. The carbon atoms C1 and C2 are pulled away from the center of the carbon cage toward the addend. It is of interest to note that two of the C−C bonds (C9−C10 and C11−C12) in the hexagon where the addend is attached are significantly shortened (1.374(5) and 1.380(5) Å). The geometry of the addend portion is similar to that found in the analogous adduct of C_{60} where addition occurs at the usual pyracylene site and the C−C distance between the affected fullerene carbon atoms is 1.596 Å.[11]

The Sc_3N unit is positioned well away from the site of external modification. Sc1 is located near a 6:5 bond with a Sc1−C14

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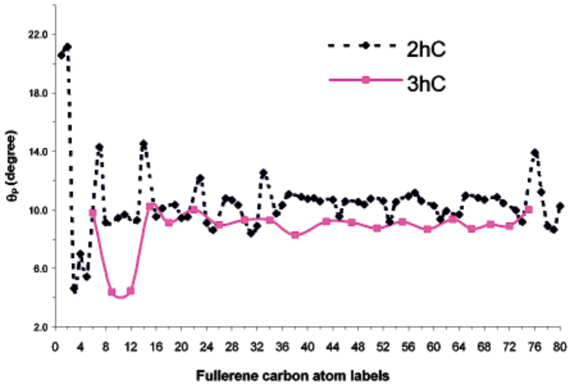

Figure 3. A plot of the pyramidalization angles (θ_p) for the fullerene carbon atoms of **1**.

distance of 2.255(4) Å and an Sc1−C33 distance of 2.282(3) Å. Sc(2) is also located over a 6:5 bond and is equidistant from C7 and C23 with Sc−C distances of 2.272(4) Å. Sc3 is 2.243(4) Å from C76 and 2.307(4) Å from C77 along another 6:5 bond. For comparison to a conventional organometallic complex, these distances are all shorter than the Sc−C distances (2.320(9), 2.357(9) Å) in the olefin complex $[(Cp^*SiNR)(PMe_3)Sc]_2(\mu_2, \eta^2,\eta^2\text{-}C_2H_4)$.[13] The Sc_3N unit is planar with the sum of N−Sc bond angles equal to 359.84°. The N−Sc distances, 2.032(3), 2.020(3), and 2.029(3) Å, are slightly longer than those in $Sc_3N@C_{80}$ (2.011(19), 1.966(12) Å)[3] and $ErSc_2N@C_{80}$ (1.968(6) Å).[7] For comparison, the Sc−N distance in dichlorobis(tetrahydrofuran)bis{(trimethylsilyl)amido}scandium is longer, 2.039 Å.[13] Theoretical calculations predicated closest Sc−C distances of 2.320 Å and Sc−N distances in the range of 2.014−2.029 Å.[14] There is a small degree of disorder in the positions of the scandium ions. Three additional positions for scandium ions have been located and found to have 0.049 site occupancy for each position. These sites are arranged at the corners of a nearly equilateral triangle.

A plot of the pyramidalization angles, θ_p,[14] (θ_p for graphite = 0°; θ_p for C_{60} = 11.6°) for the individual fullerene carbons of **1** is shown in Figure 3. The data are divided into two groups for carbon atoms at the intersection of three hexagons (3hC) and carbon atoms at the intersection of two hexagons and a pentagon (2hC). In general, the 2hC carbons atoms are more pyramidalized that the 3hC carbon atoms. The plot clearly shows that carbon atoms C1 and C2, which are directly connected to the addend, are the most pyramidalized. While the C1−C2 bond is pulled away from the cage, the remaining three carbon atoms, C3, C4, and C5, of the adjacent pentagon and two of the 3hC carbon atoms at the hexagon adjacent to the C1−C2 bond are significantly less pyramidalized than the other fullerene carbon atoms.

The location of the Sc_3N unit also produces a distortion of the C_{80} cage. Pyramidalization angles of ∼14° are observed at the carbon atoms (C7, C14, and C76) that are closest to the three scandium ions. Despite the fact that C7 and C23 are equidistant from Sc2, the pyramidalization at C7 ($\theta_p = 12.2°$) is greater than that at C23 ($\theta_p = 10.8°$). Sc2 is positioned closer to the C14 than to C33, and the pyramidalization at C14 ($\theta_p = 14.5°$) is greater than that at C33 ($\theta_p = 12.5°$). For Sc3, because of its main positioning over the top of C76 with $\theta_p = 13.9°$, the θ_p at C77, is even smaller (11.2°).

In conclusion, the structure of a covalent adduct of $Sc_3N@C_{80}$ shows that cycloaddition occurs at a C−C bond of 6:5 ring junction, and that the fullerene C1−C2 bond is elongated and pulled out from the fullerene. The Sc_3N unit is positioned away from the site of addition and causes the carbon atoms immediately neighboring the scandium atoms to protrude slightly from the surface of the fullerene cage.

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Supporting Information Available: Details of the X-ray crystallographic data collection and structure refinement, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for **1**·2 (C_6H_6) in CIF format. A Schlegel diagram showing the numbering for I_h C_{80} (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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(9) Black crystals of **1**·2 (C_6H_6) were obtained by slow evaporation of 0.5 mg of **1** in 1 mL of benzene and a drop of methanol over 7 days. Crystal data for **1**·2 (C_6H_6): black bipyramid, 0.06 mm × 0.11 mm × 0.10 mm, monoclinic, space group $P2_1/n$, $a = 19.972(7)$ Å, $b = 14.196(5)$ Å, $c = 20.986(8)$ Å, $\beta = 117.548(11)°$,$V = 5275(3)$ Å^3, $\lambda = 0.71073$ Å, $Z = 4$, $D_c = 1.801$ Mg m^{-3}; μ(Mo Kα) = 0.451 mm^{-1}; ω scans, $2\theta_{max} = 31.51°$; $T = 91(2)$ K.; 70657 refl. collected; 16838 independent ($R_{int} = 0.2438$) included in the refinement; min/max transmission = 0.952/0.973; Direct and difference Fourier methods solution (SHELXS-97, Sheldrick, 1990); full-matrix least-squares based on F^2 (SHELXL-97; Sheldrick, 1998); R1 = 0.2161, wR2 = 0.1513 for all data; conventional R1 = 0.0643 computed for 6304 observed data ($I > 2\sigma(I)$) with 0 restraints and 985 parameters. Hydrogen atoms were added geometrically and refined using a riding model. Three minor scandium sites with a refined occupancy of 0.049(1) were assigned isotropic thermal parameters.
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