Isolation and Structural Characterization of the Endohedral Fullerene $Sc_3N@C_{78}$**

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Although fullerenes with metals encapsulated within a cage of carbon atoms have been known since the beginning of fullerene chemistry,[1] progress in exploring their chemical, physical, and structural properties has been limited by the low yields of the endohedral fullerenes produced. Conducting the normal Krätschmer–Huffman arc method for fullerene preparation using graphite rods doped with trivalent metal oxides in a dynamic atmosphere that contains dinitrogen and helium results in the enhanced production of endohedral fullerenes. A recently reported example is the preparation of $Sc_3N@C_{80}$, which contains a planar Sc_3N unit within a fullerene cage of I_h symmetry.[2, 3] Performing this trimetallic nitride template (TNT) process with scandium(III)oxide doped graphite rods yields not only $Sc_3N@C_{80}$ but two other novel endohedral products: $Sc_3N@C_{68}$, in which the carbon cage must violate the isolated pentagon rule,[4] and $Sc_3N@C_{78}$. The three fullerenes were isolated in relative yields of 8:1:1, respectively; $Sc_3N@C_{78}$ is more abundant than any of the other conventional metallofullerenes such as $Sc_2@C_{84}$. These isomers have been isolated through a three-step high-pressure liquid chromatography (HPLC) procedure.[5] Figure 1 shows the mass spectra of the purified samples of the three endohedral fullerenes, along with color photographs of solutions of them in carbon disulfide. Note that each different cage imparts a distinctive color to the sample. The UV/Vis absorption spectrum of air-stable $Sc_3N@C_{78}$ in carbon disulfide is shown in Figure 2. Prominent maxima are seen at 460 and 623 nm with shoulders at longer wavelengths. Here we report the detailed structural characterization of $Sc_3N@C_{78}$. Endohedral fullerenes with a C_{78} cage are uncommon and to our knowledge none have been isolated as yet in significant quantities.

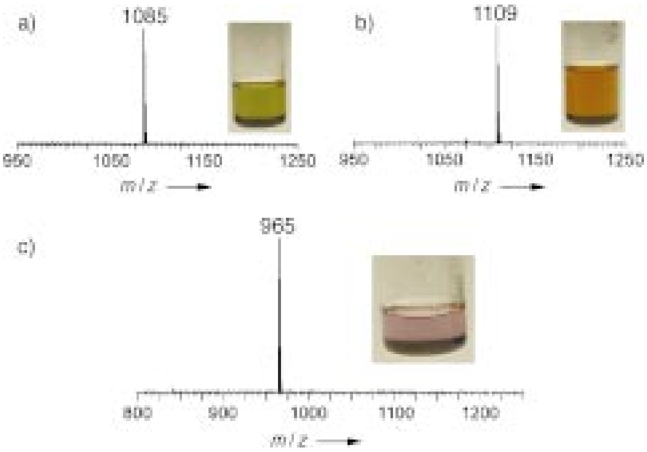

Figure 1. Mass spectra of purified samples of $Sc_3N@C_{78}$ (a); $Sc_3N@C_{80}$ (b); and $Sc_3N@C_{68}$ (c). The insets show the colors of solutions of the respective samples in carbon disulfide.

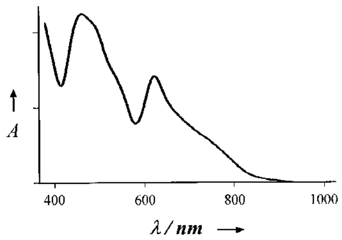

Figure 2. The UV/Vis spectrum of $Sc_3N@C_{78}$ in carbon disulfide.

There are five isomers for the empty C_{78} cage itself (with symmetries D_3(78:1), C_{2v}(78:2), $C_{2v'}$(78:3) (two distinct isomers), D_{3h}(78:4), and $D_{3h'}$(78:5) (two distinct isomers)) which obey the isolated pentagon rule.[6] Three of these five isomers have been isolated.[7–9] These isomers have been identified as having D_3, C_{2v}, and $C_{2v'}$ symmetry on the basis of their ^{13}C NMR spectra. The relative yields of the three isomers have been shown to depend on the helium pressure during the synthesis.[10] Theoretical calculations indicate that the potential energies of the five isomers increase in the following order: $C_{2v'}(78{:}3) < C_{2v}(78{:}2) < D_3 < D_{3h}(78{:}4) < D_{3h'}(78{:}5)$.[11, 12] Thus, the three most stable isomers have been separated and identified while the two highest energy isomers, both with D_{3h} symmetry, have not yet been found in conventionally prepared fullerene soot.

Black crystals of $Sc_3N@C_{78} \cdot [Co(oep)] \cdot 1.5\,C_6H_6 \cdot 0.3\,CHCl_3$ (**1**, oep = octaethylporphyrin) were obtained by the slow diffusion of solutions of $Sc_3N@C_{78}$ in benzene and $[Co^{II}(oep)]$ in chloroform.[13] Figure 3 shows a diagram of the individual molecular components. The fullerene is cradled within the cavity provided by the cobalt porphyrin and its eight ethyl groups. The dimensions of the non-fullerene components are entirely normal.

The fullerene component suffers from disorder, which has been satisfactorily modeled. Three orientations of the C_{78} cage, which has been treated as a rigid group with $D_{3h'}$(78:5) geometry (with the central [6,6] ring junctions of pyracylene patches lying in the horizontal mirror plane) using idealized coordinates, have been found with relative site occupancies of 0.25, 0.15, and 0.10. Since the fullerene is situated on a mirror

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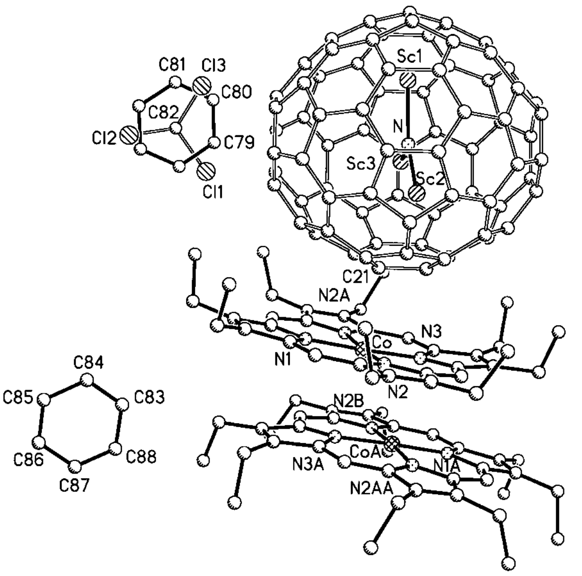

Figure 3. A view of the structure of **1** that shows the relative orientation of all the components. Only the major (0.25 %) orientation of the Sc$_3$N@C$_{78}$ molecule is shown. At one site, which is partially occupied by 0.5 benzene and 0.3 chloroform molecules (top left), the two molecules are shown superimposed.

plane that does not coincide with any of the mirror planes of the C$_{78}$ cages, each of these orientations also generates a second C$_{78}$ cage. Three orientations of the Sc$_3$ portion have also been identified with fractional occupancies again of 0.25, 0.15, and 0.10.

Figure 4 shows two orthogonal views of the Sc$_3$N@C$_{78}$ molecule in its major orientation. The N−Sc distances are 1.988(7) (Sc1), 1.983(15) (Sc2), and 2.125(5) Å (Sc3), and the Sc-N-Sc angles are Sc1-N-Sc2 130.3(5), Sc1-N-Sc3 113.8(5), and Sc2-N-Sc3 115.9(5)°. The flat Sc$_3$N portion is oriented so that the it lies near the horizontal mirror plane of the C$_{78}$ cage. In this orientation each scandium atom lies over a [6,6] ring junction within a pyracylene patch. The shortest C−Sc distances fall in a narrow range: Sc1-C37 2.058(3), Sc1-C38 2.107(3), Sc2-C6 2.058(16), Sc2-C7 2.024(16), Sc3-C66 2.075(4), and Sc3-C67 2.106(5) Å.

All five isomeric C$_{78}$ cages have been examined within the model described above, and the D_{3h}(78:5) isomer clearly produces the best fit. For example, although the C_{2v}(78:3) isomer differs from the D_{3h}(78:5) isomer only by a single Stone–Wales transformation[14] (which involves reorientation of the inner C−C bond in a pyracylene patch) introduction of the C_{2v}(78:3) isomer into the major orientation results in an increase in the R factor by about 2 % and in a much less uniform distribution of the thermal ellipsoids throughout the C$_{78}$ cage. Introduction of other isomers produces even poorer agreement with the data.

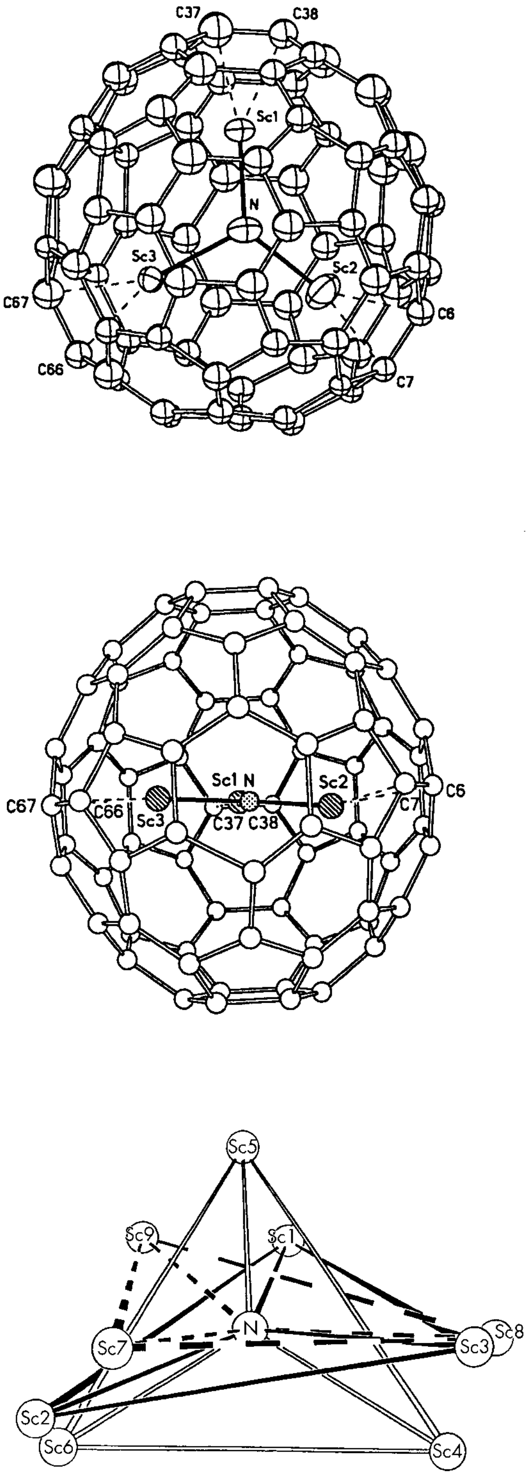

Figure 4. Two orthogonal views of the major form (0.25 site occupancy) of the Sc$_3$N@C$_{78}$ molecule in **1**, and a digram showing the relative ortientations of the three different triangular Sc$_3$ units.

Figure 4 also shows the relative orientations of the three different Sc$_3$ subunits. Significantly, all three orientations of the Sc$_3$N group have analogous dispositions and dimensions with regard to the three different orientations of the C$_{78}$ cage. Thus the threefold axis of the major orientation of the C$_{78}$ cage makes an angle of 5.9° with the normal to the Sc1-Sc2-Sc3 plane, while the threefold axes of the C$_{78}$ cages with 0.15 and 0.10 occupancy make angles of 9.6 and 9.9°, respectively with the normal to the Sc4-Sc5-Sc6 and Sc7-Sc8-Sc9 plane, respectively. It is particularly important to note that in each of these orientations the Sc$_3$N portion lies near the horizontal mirror plane of the C$_{78}$ cage, and each scandium ion is situated over two carbon atoms at [6,6] ring junctions within pyracylene patches of the cage. Such sites are completely analogous to the sites where metal atoms coordinate on the outside of fullerenes.[15, 16] This orientation differs from that seen in $ErSc_2N@C_{80}$ and $Sc_3N@C_{80}$ where the metal atoms are located closest to individual carbon atoms of the icosahedral C_{80} cage.[17] However, the C_{80} cage with I_h symmetry lacks any pyracylene patches, and the Sc–C interactions seen in $Sc_3N@C_{78}$ are impossible for this C_{80} cage. Consequently, $Sc_3N@C_{78}$, with the metal ions centered above [6,6] ring junctions within pyracylene patches, provides a better paradigm for metal ion/fullerene interactions than does $Sc_3N@C_{80}$.

After completion of the X-ray crystallographic analysis, the 125.78 MHz ^{13}C NMR spectrum of $Sc_3N@C_{78}$ was obtained in CS_2/10 % [D_6]acetone (9:1) with $[Cr(acac)_3]$ (acac = acetylacetanoate anion) as a relaxation reagent. As expected for a cage with D_{3h} symmetry, eight lines (three with half intensity) were observed at $\delta = 155.60$ (1), 151.23 (0.5), 150.50 (1), 143.16 (0.5), 142.48 (1), 135.34 (1), 133.84 (0.5), 132.97 (1) (relative intensity).

With the knowledge that $Sc_3N@C_{78}$ has a C_{78} cage with D_{3h} symmetry, it is now clear that the TNT process generates carbon-cage isomers in each of the three new products– -$Sc_3N@C_{80}$, $Sc_3N@C_{68}$, and $Sc_3N@C_{78}$—that are different from the isomers of the corresponding empty cage fullerenes. Thus $Sc_3N@C_{80}$ exists with an I_h cage, whereas empty C_{80} has been found to exist as the D_2 and D_{5d} isomers;[18, 19] $Sc_3N@C_{78}$ has a D_{3h} cage, while empty C_{78} has been isolated as the D_3 and two C_{2v} isomers; and finally although $Sc_3N@C_{68}$ exists, no empty cage C_{68} is formed in the conventional fullerene preparations.[20]

Experimental Section

Cored graphite rods (6-mm diameter) were filled with CoO (180 mg) and a mixture of Sc_2O_3 and graphite powder (4/96 w/w). These rods were vaporized in a Krätschmer–Huffman electric-arc generator under a dynamic atmosphere of He/N_2 (1250/20 mL min^{-1}). The resulting soot from four graphite rods was extracted with cold CS_2 to yield a soluble extract (200 mg) of fullerenes and endohedral metallofullerenes. After chromatographic isolation, 1–2 mg (0.5–1 % yield of soluble extract) of purified $Sc_3N@C_{78}$ was obtained with an overall yield from the total available carbon (graphitic powder and rods) of about 0.2 %.

Crystals of **1** were obtained by layering a green solution of about 0.5 mg of $Sc_3N@C_{78}$ in 0.5 mL of benzene over a red solution of 2.5 mg of $[Co^{II}(oep)]$ in 1.5 mL of chloroform. The two solutions were allowed to diffuse together over five days and black crystals gradually formed.

Crystal data for **1**: black parallelepiped, $0.08 \times 0.08 \times 0.05$ mm^3, monoclinic, space group $C2/m$, $a = 25.124(2)$, $b = 14.9400(13)$, $c = 19.533(2)$ Å, $\beta = 93.720(2)^\circ$, $V = 7316.3(11)$ Å^3, $\lambda = 0.77490$ Å, $Z = 4$, $\rho_{calcd} = 1.662$ Mg m^{-3}; μ(16 KeV) = 2.16 mm^{-1}; ω scans, $2\Theta_{max} = 61.6^\circ$; $T = 110(2)$ K; 41 718 reflexes collected; 7058 independent ($R_{int} = 0.056$) included in the refinement; min/max transmission = 0.85/0.92; Patterson and difference Fourier methods solution (SHELXS-97, Sheldrick, 1990); full-matrix least squares based on F^2 (SHELXL-97; Sheldrick, 1998); $R = 0.1175$, $wR = 0.3026$ for all data; conventional $R1 = 0.1107$ computed for 7058 observed data ($> 2\sigma(I)$) with 27 restraints and 404 parameters. The data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), which is funded by the U.S. Department of Energy and the National Institute of Health. The diffractometer employed a Huber Kappa goniometer and Area Detector Systems Corp 2×2 matrix Quantum-4 CCD detector. The monochromator was a double-crystal "pin-post" type. Two runs were merged and scaled. The first run used 0.5° ϕ scans of 1 s exposure at a detector distance of 80 mm. The second run used 2 s exposures and a 70 mm distance. The fullerene molecule was refined as a rigid group in three different orientations by using idealized coordinates. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148633. 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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