A Scandium Carbide Endohedral Metallofullerene: $(Sc_2C_2)@C_{84}$**

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The recent discovery of single-wall carbon nanotubes with C_{60}[1] inside the tubular hollow space has demonstrated that such a large empty space can actually encapsulate fullerenes and carbon-related molecules. However, in the fullerene size range, only metal atoms,[2] metal clusters,[3] metal nitrides,[4a] nitrogen atoms,[4b–d] and noble gas atoms[5] are observed to be encaged inside C_{60}, C_{70}, or higher fullerenes. Experimental evidence that carbon atoms or metal–carbon clusters (carbides) can be encapsulated inside fullerenes has not yet been reported. Here we report the production, isolation, and structural and spectroscopic characterization of the first scandium carbide endohedral fullerene $(Sc_2C_2)@C_{84}$.[6] The endohedral nature and detailed molecular/crystal structure of the carbide Sc_2C_2 in the D_{2d}-C_{84} cage were revealed by both ^{13}C NMR and synchrotron X-ray structural analyses.

The relative yield of $(Sc_2C_2)@C_{84}$ is about 2% of that of C_{60}, which is lower than those of the most abundant discandium metallofullerenes $Sc_2@C_{84}$ and $Sc_2@C_{82}$, but higher than those of all other metallofullerenes. We were able to isolate 3.5 mg of $(Sc_2C_2)@C_{84}$ as a black powder for spectroscopic and structural studies. Purified $(Sc_2C_2)@C_{84}$ is stable in air and soluble in normal organic solvents such as toluene and carbon disulfide. It has a light green color in CS_2 solution,. Figure 1 shows the UV/Vis/NIR absorption spectrum of $(Sc_2C_2)@C_{84}$ between 400 and 2000 nm in CS_2 solution. A strong absorption band is observed around 600 nm, and the absorption onset is at 1410 nm. The overall absorption spectrum is quite different from those of the seven empty C_{84} fullerene isomers[7] and the three $Sc_2@C_{84}$ isomers[2].

To obtain structural information on $(Sc_2C_2)@C_{84}$, ^{13}C NMR measurements were performed using a Varian Inova-600 spectrometer at a ^{13}C frequency of 125 MHz (CS_2 solution, $[Cr(acac)_3]$ relaxant, $[D_6]$acetone lock). Figure 2 shows a typical ^{13}C NMR spectrum of $(Sc_2C_2)@C_{84}$ obtained after

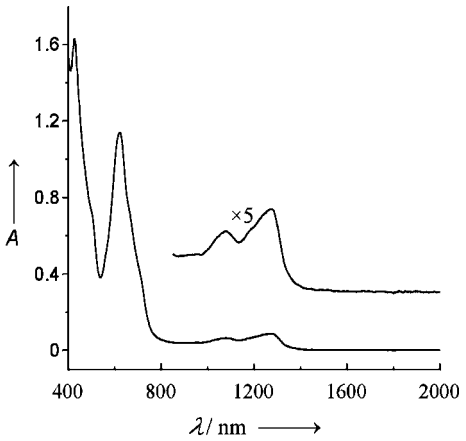

Figure 1. UV/Vis/NIR spectrum of purified $(Sc_2C_2)@C_{84}$ in CS_2 solution. The strong absorption band at around 600 nm results in a light green color. A = absorbance.

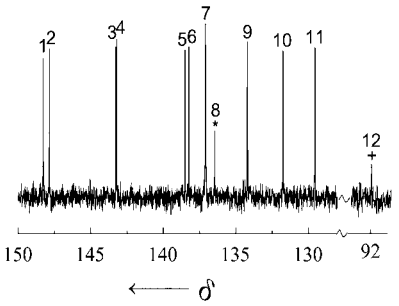

Figure 2. ^{13}C NMR spectrum (171 000 scans, 240 h) of $(Sc_2C_2)@C_{84}$ in CS_2 solution (2.5 mg $[Cr(acac)_3]$ (acac = acetylacetonate) as relaxant, and $[D_6]$acetone as reference). The measured chemical shifts δ and relative intensities I_{rel} are: 1 ($\delta = 148.27$, $I_{rel} = 18.0$), 2 (147.85, 19.3), 3 (143.27, 19.6), 4 (143.21, 20.6), 5 (138.50, 19.2), 6 (138.24, 19.6), 7 (137.09, 22.6), 8* (136.50, 8.5), 9(134.20, 20.3), 10 (131.75, 19.1), 11 (129.55, 19.5), 12^+ (91.99, 4.5). Lines 8 and 12 have 1/2 and 1/4, respectively, of the intensity of the other ten lines.

171 000 scans (240 h) at room temperature. The spectrum consists of a series of ten distinct lines of nearly equal intensity, one line with half the intensity, and an additional line with 1/4 the intensity. The ^{13}C NMR pattern is thus assigned as $(10 \times 8;\ 1 \times 4;\ 1 \times 2)$, where $(a \times b)$ indicates ([number of NMR lines] × [relative intensity]).[8] A wider spectral range revealed no other peaks besides these 12 signals, and this confirms the high purity of the sample. C_{86} has 19 isomers satisfying the isolated pentagon rule (IPR).[8] However, even the most symmetrical isomer of D_3-C_{86} requires 15 $(1 \times 2;\ 14 \times 6)$ ^{13}C NMR signals. The current ^{13}C NMR spectrum with only 12 lines can not be assigned to $Sc_2@C_{86}$.

Eleven of the 12 ^{13}C NMR signals are in the range for sp^2-hybridized fullerene C atoms ($\delta = 129.55 - 148.27$), and the other is in the range for a sp-hybridized carbon atom ($\delta = 92$). The presence of such an NMR line indicates that this metallofullerene is not a normal C_{86}-based metallofullerene. In fact, the observed NMR spectrum in the sp^2 fullerene range is quite similar to that of D_{2d}-C_{84},[9] which exhibits eleven NMR lines with a $(10 \times 8;\ 1 \times 4)$ pattern. This observation strongly suggests that the present metallofullerene is not $Sc_2@C_{86}$ but $(Sc_2C_2)@C_{84}$, in which a Sc_2C_2 cluster is encaged

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by a D_{2d}-C_{84} fullerene. The NMR lines 1–11 in Figure 2 are due to the D_{2d}-C_{84} (no. 23)[9] cage, and line 12 results from the Sc_2C_2 cluster (^{13}C NMR pattern: 2×1).

We performed synchrotron X-ray diffraction on the powder sample to confirm the endohedral structure of $(Sc_2C_2)@C_{84}$,. The space group of the crystal was assigned as cubic $Fm\bar{3}m$ ($a = 15.8644(4)$ Å). The experimental data were analyzed by the MEM/Rietveld method, which was successfully applied to the structure determination of metallofullerenes such as $Y@C_{82}$,[10a] $Sc@C_{82}$,[10b] $Sc_2@C_{84}$,[10c] and $Sc_3@C_{82}$.[3] The number of structure factors derived in this analysis was 36. The reliabilty factors are $R_I = 0.024$ and $R_{wp} = 0.021$, which are much better than those of previous studies on the metallofullerenes. The MEM analysis was carried out with $128 \times 128 \times 128$ pixels per unit cell. The reliability factor of the final MEM charge density was $R = 0.017$.

The MEM charge density is shown in Figure 3 as an equicontour surface for a section of the molecular structure. Several maxima in the charge density were found inside the carbon cage. The MEM charge density also reveals that the C_{84} cage has D_{2d} (no. 23) symmetry and that the C_2 axis is parallel to the ⟨100⟩ fcc direction of the unit cell. As a result of the site symmetry of $4mm$, the C_2 axis of $(Sc_2C_2)@C_{84}$ is oriented in six equivalent ⟨100⟩ directions and show a merohedral disorder. From Figure 3, which exhibits the section through the Sc atoms and C atoms in four positions among the six equivalent positions, it is concluded that the Sc_2C_2 cluster is encapsulated in the D_{2d}-C_{84} fullerene cage.

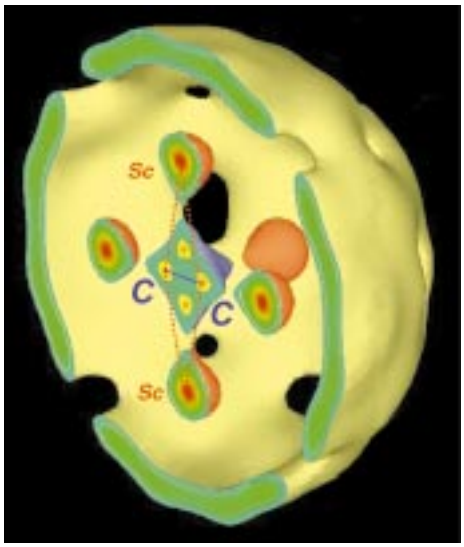

Figure 3. Half section of the equicontour (1.9 e Å^{-3}) surface of the MEM charge density for $(Sc_2C_2)@C_{84}$. The cross section corresponds to the (100) plane. The charge-density surfaces of the Sc and C atoms are colored red and blue, respectively. The Sc_2C_2 cluster is emphasized by dotted red lines and a solid blue line. In the cubic symmetry, the $(Sc_2C_2)@C_{84}$ molecules exhibit merohedral disorder in the unit cell, and an Sc_2C_2 cluster thus represents the disordered feature along the [100], [010], and [001] directions with respect to the fullerene cage.

The observation of a single NMR line due to a sp-hybridized carbon atom ($\delta = 92$) for Sc_2C_2 (see Figure 2) suggests that the Sc_2C_2 cluster is in a rapid rocking motion along the Sc–Sc axis between two mutually orthogonal positions. This is consistent with the moderate smearing of charge density of the central C_2 moiety around the Sc–Sc axis in Sc_2C_2 (see Figure 3). Figure 4 shows a one-dimensional section of the charge density along the center axis of the molecule, which passes through the density maxima.The four internal maxima are identified from the charge density concentration at the density maxima as Sc and C atoms. This assignment reveals that a Sc_2C_2 carbide cluster is indeed encapsulated in a C_{84} cage. The Sc_2C_2 form of scandium carbide has not been found in solid scandium carbides. The composition of the known scandium carbides in the solid state are Sc_4C_3, $Sc_{13}C_{10}$, and $Sc_{15}C_{19}$.[11]

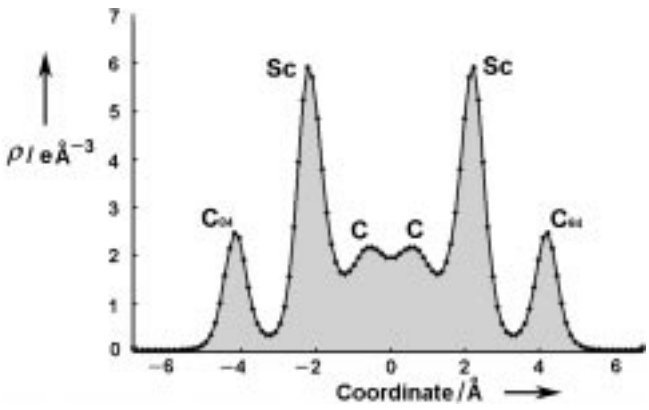

Figure 4. One-dimensional MEM charge density along the ⟨100⟩ direction, which passes through the center of the $(Sc_2C_2)@C_{84}$ molecule. Because of the merohedral disorder (see text), two carbon density maxima are seen along this bisecting axis (see Figure 3).

The molecular structure based on the above analysis is presented in Figure 5. The Sc···Sc and C···C distances of the Sc_2C_2 cluster are 4.29(2) Å and 1.42(6) Å, respectively. The C–C distance lies between those of typical single and double bonds, and is very similar to that of the C–C bond (1.43 Å) that connects two pentagons on a C_{60} molecule.[12] The Sc–C

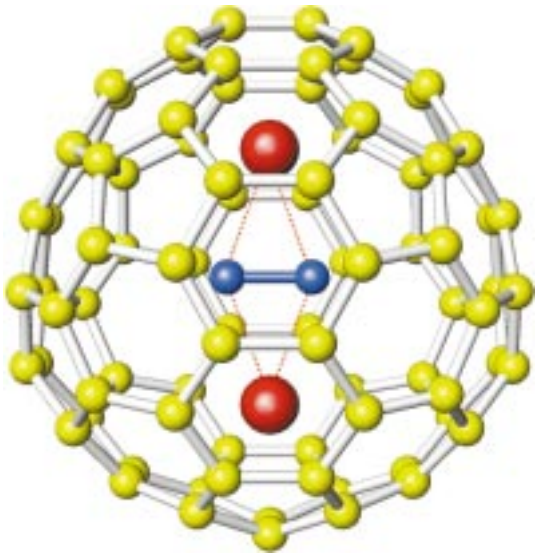

Figure 5. Schematic representation of the $(Sc_2C_2)@C_{84}$ molecule based on the results of the synchrotron X-ray powder diffraction and ^{13}C NMR experiments.

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distance is 2.26(3) Å, which is qualitatively the same as an ab initio theoretical Sc–C bond length (2.135 Å) of a ScC_2 cluster.[13] The number of electrons belonging to the Sc_2C_2 cluster is estimated to be 51.9(2) e from the MEM charge density; hence, the Sc_2C_2 species is in the divalent charge state in the C_{84} fullerene cage. The formal electronic structure of $(Sc_2C_2)@C_{84}$ can thus be described as $(Sc_2C_2)^{2+}@C_{84}^{2-}$. The nature of the bonding between Sc and C_2 might be highly ionic as in the case of the ScC_2 cluster.[13a] As one of the two major isomers of C_{84} (namely, D_2 and D_{2d}), D_{2d}-C_{84} not only has much higher abundance than the other C_{84} isomers,[7] but also has an unique ability to encage both metal atoms to form $Sc_2@C_{84}$,[10c] and metal carbide clusters to form $(Sc_2C_2)@C_{84}$.

Experimental Section

The details of the production, separation, and isolation of endohedral scandium fullerenes has been described elsewhere.[2, 14, 15] Briefly, soot containing $(Sc_2C_2)@C_{84}$ and other scandium metallofullerenes such as $Sc_2@C_{84}$[15] and $Sc_2@C_{82}$[14] was generated in a direct-current (350 A, 21 V) arc discharge of Sc_2O_3/graphite composite rods ($12 \times 12 \times 300$ mm, 0.8 atom %, heat treated at 1600 °C, Toyo Tanso Co.) under a 17 L min^{-1} flow of helium at 50 – 100 Torr. The soot was Soxhlet-extracted with carbon disulfide for 12 h. $(Sc_2C_2)@C_{84}$ was isolated by multistage high performance liquid chromatography (HPLC)[2, 14, 15] with two complementary 5PYE (21×250 mm) and Buckyclutcher (21×500 mm) columns. Stage 1 was HPLC on a 5PYE column, which was used primarily to remove C_{60} and C_{70}. In stage 2, the $(Sc_2C_2)@C_{84}$-containing fraction (yellow) collected in stage 1 was re-injected into the 5PYE column, and recycling HPLC was performed. After a few cycles, the $(Sc_2C_2)@C_{84}$ sub-fraction containing some $Sc_2@C_{82}$ and C_{90} was collected. In stage 3, recycling HPLC on a Buckyclutcher column was employed to completely separate $(Sc_2C_2)@C_{84}$ from the other fullerenes. Stages 2 and 3 were repeated several times to increase the sample purity to 99 %, as confirmed by laser-desorption time-of-flight (LD-TOF) mass spectrometry.

Solvent-free $(Sc_2C_2)@C_{84}$ powder sample was sealed in a silica-glass capillary (0.3 mm inside diameter). To collect an X-ray powder pattern with good counting statistics, a synchrotron radiation (SR) X-ray powder experiment with an imaging plate (IP) as a detector was carried out at SPring-8 BL02B2. The exposure time on the IP was 80 min. The wavelength of incident X-rays was 0.75 Å. The X-ray powder pattern of $(Sc_2C_2)@C_{82}$ was obtained in 0.02° steps in the range $3.0 \leq 2\theta \leq 30.5°$, which corresponds to 1.45 Å resolution in the *d* spacing.

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A Two-Dimensional Polyrotaxane with Large Cavities and Channels: A Novel Approach to Metal – Organic Open-Frameworks by Using Supramolecular Building Blocks**

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Dedicated to Professor James A. Ibers on the occasion of his 70th birthday

Mechanically interlocked supermolecules such as rotaxanes and catenanes have received much attention because of their intriguing structures as well as their potential applications.[1, 2] We have been interested in the self-assembly of such

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