Endohedral Fullerenes

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Experimental and Theoretical Studies of the Scandium Carbide Endohedral Metallofullerene $Sc_2C_2@C_{82}$ and Its Carbene Derivative**

Yuko Iiduka, Takatsugu Wakahara, Koji Nakajima, Tsukasa Nakahodo, Takahiro Tsuchiya, Yutaka Maeda, Takeshi Akasaka,* Kenji Yoza, Michael T. H. Liu, Naomi Mizorogi, and Shigeru Nagase*

Endohedral metallofullerenes have attracted special attention as new spherical molecules with unique properties that are unexpected for empty fullerenes.[1–3] Much work has been carried out on metallofullerenes with Sc, Y, and La atoms encapsulated inside C_{82} and C_{84} cages. Among these, scandium carbide endohedral metallofullerenes, such as $Sc_2C_2@C_{84}$[4,5] and $Sc_3C_2@C_{80}$,[6,7] are the most interesting because of the encapsulation of the C_2 unit together with several metal atoms, which is very important to the chemistry of scandium carbide endohedral metallofullerenes. For the Sc_2C_{84} metallofullerene, three isomers (I, II, and III) have been isolated.[8,9] The most abundant isomer, Sc_2C_{84}(III), was characterized and discussed in terms of its X-ray photoelectron,[10] ^{13}C NMR,[9] ^{45}Sc NMR,[11] IR,[12] and Raman[13] spectroscopic measurements, powder X-ray analysis,[14] and theoretical calculations[15] on the premise that two Sc atoms were encapsulated inside the D_{2d} isomer of C_{84}. However, we have very recently observed an improved ^{13}C NMR spectrum of Sc_2C_{84}(III) that shows a total of 17 lines (11 full-intensity signals, five half-intensity signals, and one 1/6-intensity signal),[16] unlike the previous ^{13}C NMR study.[9] The newly observed ^{13}C NMR pattern is not explained by placing two Sc atoms inside any of the isomers of C_{84} that satisfy the isolated-pentagon rule. We have suggested that the ^{13}C NMR pattern is explained by the fact that two C atoms as well as two Sc atoms are encapsulated inside the C_{3v} isomer of C_{82}. Very recently, it has been found that the $Sc_2C_2@C_{82}$ structure is correct by MEM (maximum-entropy method)/Rietveld analysis of synchrotron X-ray powder diffraction data, though the $Sc_2@C_{84}$ structure was once determined by MEM/Rietveld analysis.[17]

To verify that Sc_2C_{84}(III) is a scandium carbide metallofullerene ($Sc_2C_2@C_{82}$(III)), X-ray single-crystal analysis and density functional calculations were carried out. The structure of $Sc_2C_2@C_{82}$(III), optimized by density functional calculations, is shown in Figure 1.[18] The electronic structure is described as $(Sc_2C_2)^{4+}C_{82}^{4-}$ as a result of four-electron transfer from Sc_2C_2 to C_{82}. The structure is most stable when the encapsulated Sc_2C_2 moiety has a bent structure and two Sc atoms are not equivalent. This result seems contradictory to the ^{13}C NMR spectrum (16 signals), which shows that $Sc_2C_2@C_{82}$(III) has C_{3v} symmetry, and the ^{45}Sc NMR spectrum (only one signal), which shows that the two Sc atoms are equivalent. This situation is explained by the fact that the Sc and C atoms in Sc_2C_2 are allowed to rotate and move rapidly on the NMR time scale. The redox potentials of $Sc_2C_2@C_{82}$(III), measured by cyclic voltammetry (CV) and

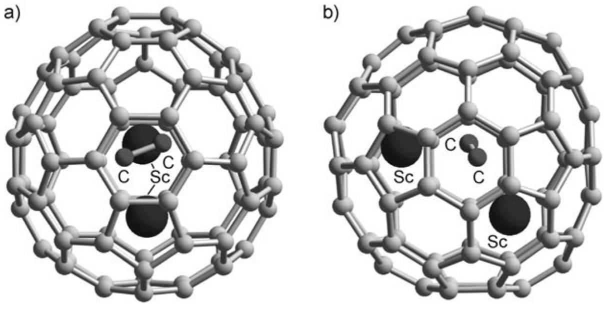

Figure 1. The optimized structure of $Sc_2C_2@C_{82}$(III); a) front view, b) side view.

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[*] Y. Iiduka, Dr. T. Wakahara, K. Nakajima, Dr. T. Nakahodo, Dr. T. Tsuchiya, Prof. Dr. T. Akasaka
Center for Tsukuba Advanced Research Alliance
University of Tsukuba
Tsukuba, Ibaraki 305-8577 (Japan)
Fax: (+81) 29-853-6409
E-mail: akasaka@tara.tsukuba.ac.jp
Homepage: http://www.tara.tsukuba.ac.jp/~akasaka-lab/
Dr. N. Mizorogi, Prof. Dr. S. Nagase
Department of Theoretical Molecular Science
Institute for Molecular Science
Okazaki, Aichi 444-8585 (Japan)
Fax: (+81) 56-453-4660
E-mail: nagase@ims.ac.jp
Dr. Y. Maeda
Department of Chemistry
Tokyo Gakugei University
Koganei, Tokyo 184-8501 (Japan)
Dr. K. Yoza
Bruker AXS K. K.
Yokohama, Kanagawa 221-0022 (Japan)
Prof. Dr. M. T. H. Liu
Department of Chemistry
University of Prince Edward Island
Charlottetown, Prince Edward Island C1A4P3 (Canada)

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differential pulse voltammetry (DPV),[19] are given in Table 1 together with the calculated HOMO and LUMO levels. The reduction and oxidation potentials correlate well with the LUMO and HOMO levels, respectively. The redox potentials and HOMO–LUMO levels resemble those of diamagnetic metallofullerenes such as $Sc_3N@C_{80}$ and $La_2@C_{80}$.[20] The relatively large HOMO–LUMO gap of $Sc_2C_2@C_{82}$(III) is reflected in the low reactivity toward disilirane.[19]

Table 1: The redox potentials[a] and HOMO–LUMO levels of $Sc_2C_2@C_{82}$(III) and related endohedral fullerenes.

Compound	E_1 (ox) [V]	E_1 (red) [V]	HOMO [eV]	LUMO [eV]
$Sc_2C_2@C_{82}$(III)	+0.47	−0.94[b]	−5.30	−3.29
$Sc_2C_2@C_{82}$(III)[19]	+0.53	−0.97[b]		
$Sc_3N@C_{80}$[20]	+0.62	−1.22	−5.48	−3.14
$La_2@C_{80}$[20]	+0.56	−0.31	−5.40	−4.21

[a] Half-cell potentials unless otherwise stated; values are relative to the ferrocene/ferrocenium couple. [b] Irreversible; values were obtained by differential pulse voltammetry.

To restrain the disorder of $Sc_2C_2@C_{82}$(III) in the crystal lattice, chemical functionalization was performed by the irradiation of a *o*-dichlorobenzene/toluene solution of $Sc_2C_2@C_{82}$(III) and an excess molar amount of 2-adamantane-2,3-[3*H*]-diazirine in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 350 nm). The resultant cycloadduct of $Sc_2C_2@C_{82}$(III) and adamantylidene carbene (Ad), $Sc_2C_2@C_{82}$(Ad), was purified by preparative HPLC. MALDI-TOF mass analysis of the purified sample exhibited a single molecular ion peak.

The structure of $Sc_2C_2@C_{82}$(Ad), determined by X-ray single-crystal analysis, is shown in Figure 2. The adduct results from the 5,6-addition of Ad and has an opened structure. Obviously, the carbon cage originates from the C_{3v} isomer of C_{82} (not C_{84}). The crystal structure of $Sc_2C_2@C_{82}$(Ad) has C_1 symmetry. At 90 K, three Sc_2 pairs were observed to be disordered over several positions with occupation percentages such as 51, 40, and 9%, indicating rotation of the Sc atoms inside the C_{82} cage (see the Supporting Information). Reflecting this rotation, the ^{13}C NMR spectrum shows that $Sc_2C_2@C_{82}$(Ad) has C_s symmetry (Figure 3) and the ^{45}Sc NMR spectrum shows only one signal (see the Supporting Information). Only the Sc_2 pair with the highest occupation percentage is shown for clarity in Figure 2. Notably, the most stable structure calculated for $Sc_2C_2@C_{82}$ (Figure 1) is found in the crystal structure of $Sc_2C_2@C_{82}$(Ad) (Figure 2).

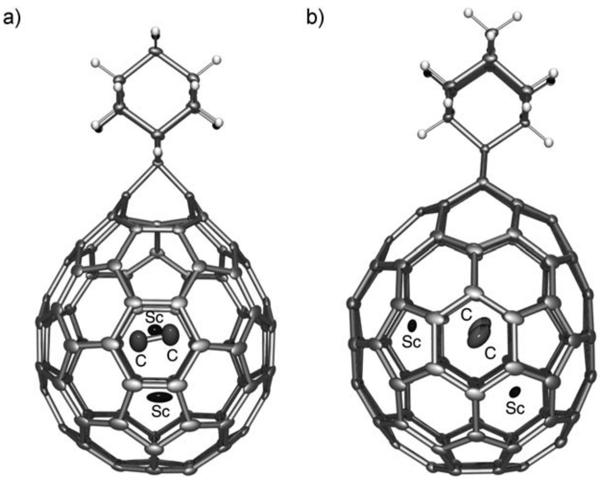

Figure 2. ORTEP drawing of $Sc_2C_2@C_{82}$(Ad) with thermal ellipsoids shown at the 50% probability level; a) front view, b) side view.

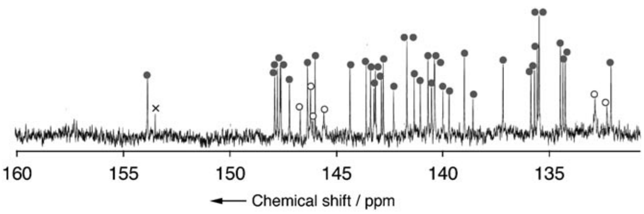

Figure 3. ^{13}C NMR spectrum of $Sc_2C_2@C_{82}$(Ad). The signals for carbon atoms encapsulated in C_{82} were not observed; ●: full intensity on C_{82} cage, ○: half intensity on C_{82} cage, ×: impurity.

X-ray crystal analysis and density functional calculations reveal that the Sc_2C_{84} metallofullerene has the form of $Sc_2C_2@C_{82}$ (and not $Sc_2@C_{84}$),[21] as suggested by our recent ^{13}C NMR study, and reveal how the scandium carbide is encapsulated inside the C_{82} fullerene.

Experimental Section

The soot containing scandium metallofullerenes was prepared according to a reported procedure.[8] Sc/C composite rods (4.7 × 10 × 150 mm^3, 2.0 atom%) were arc-vaporized at 150 A and 40 V under helium at 50 torr. The soot was collected and extracted with 1,2,4-trichlorobenzene (TCB) for 15 h. $Sc_2C_2@C_{82}$(III) was isolated from various empty fullerenes and other scandium metallofullerenes by a multistage HPLC method. A solution of $Sc_2C_2@C_{82}$(III) (2.0 mg, 0.0018 mmol) and 2-adamantane-2,3-[3*H*]-diazirine (15 mg, 0.091 mmol) in toluene/*o*-dichlorobenzene (9:1, 20 mL) was placed in a pyrex reactor, degassed by freeze–pump–thaw cycles under reduced pressure, then irradiated with a high-pressure mercury-arc lamp (cutoff < 350 nm) for 35 s. The reaction mixture was injected into a Buckyprep column, and the adduct $Sc_2C_2@C_{82}$(Ad) (**1**) was isolated. Black crystals of **1** were obtained by layering a CS_2/*o*-dichlorobenzene (1:1) solution of **1** onto dichloromethane. The ^{13}C and ^{45}Sc NMR spectra were measured on AVANCE-500 and AVANCE-600 spectrometers. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were recorded on a BAS CV50W electrochemical analyzer. A platinum disk and a platinum wire were used as the working electrode and the counter-electrode, respectively. The reference electrode was a saturated calomel electrode (SCE) filled with 0.1 M nBu_4NPF_6 in *o*-dichlorobenzene. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc^+) as the standard. CV: scan rate 20 mV s^{-1}. DPV: pulse amplitude 50 mV; pulse width 50 ms; pulse period 200 ms; scan rate 20 mV s^{-1}.

Spectral data of $Sc_2C_2@C_{82}$(Ad): MALDI-TOF MS (matrix: 1,1,4,4-tetrapenyl-1,3-butadiene) *m*/*z*: 1232 [M^+]; ^{13}C NMR (125 MHz, CS_2, 293 K): $\delta = 153.8$ (2C), 147.8 (2C), 147.7 (2C), 147.6 (2C), 147.6 (2C), 147.2 (2C), 146.7 (1C), 146.3 (2C), 146.2 (1C), 146.1 (1C), 146.6 (2C), 145.6 (1C). 144.3 (2C), 143.6 (2C), 143.4 (2C), 143.2 (2C), 143.2 (2C), 142.9 (2C), 142.8 (2C), 142.3

(2C), 141.7 (2C), 141.7 (2C), 141.4 (2C), 141.4 (2C), 140.7 (2C), 140.5 (2C), 140.4 (2C), 140.4 (2C), 140.0 (2C), 139.7 (2C), 139.0 (2C), 138.6 (2C), 137.2 (2C), 135.9 (2C), 135.7 (2C), 135.6 (2C), 135.5 (2C), 135.5 (2C), 134.5 (2C), 134.4 (2C), 134.3 (2C), 132.9 (1C), 132.4 (1C), 132.2 (2C), 37.3 (1C), 35.6(2C), 35.4 (1C), 34.3 (2C), 33.2 (1C), 28.1 (2C). The signals for the carbon atoms encapsulated in C_{82} and quaternary carbon atoms on the adamantyl moiety were not observed. A capillary containing [D$_6$]acetone was used as an internal lock. ^{45}Sc NMR (145.8 MHz, CS_2/[D$_4$]*o*-dichlorobenzene, 293 K): $\delta = 220$ ppm; the chemical shift scale was calibrated using Sc_2O_3 in HCl/D_2O as an external reference (0 ppm).

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