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Entrapped Bonded Hydrogen in a Fullerene: the Five-Atom Cluster Sc₃CH in C₈₀

Matthias Krause,[a] Frank Ziegs,[a] Alexey A. Popov,[a, b] and Lothar Dunsch*[a]

The synthesis and characterisation of the new endohedral cluster fullerene Sc₃CH@C₈₀ is reported. The encapsulation of the first hydrocarbon cluster inside a fullerene was achieved by the arc burning method in a reactive CH₄ atmosphere. The extensive characterisation by mass spectrometry (MS), high- pressure liquid chromatography (HPLC), ⁴⁵Sc NMR, electron spin resonance (ESR), UV/Vis-NIR and Raman spectroscopy provided the experimental evidence for the caging of the five-atom Sc₃CH cluster inside the C₈₀ cage isomer with icosahedral symmetry. The proposed new structure was confirmed by DFT calculations, which gave a closed shell and large energy gap structure. Thus a pyramidal Sc₃CH cluster and the I_h-C₈₀ cage were shown to be the most stable configuration for Sc₃CH@C₈₀ whereas alternative structures give a smaller bonding energy as well as a smaller energy gap.

Introduction

The cavity of a fullerene is predestined for the inclusion of atoms, ions or clusters, with hydrogen encapsulation being one of the preparative challenges in carbon nanostructure research. For many years, the latter was considered to be impossible due to the high mobility of hydrogen. Recently, Komatsu and co-workers have been successful in including molecular hydrogen via a multistage synthetic route of opening the carbon cage, high-pressure (560 atm) incorporation of molecular hydrogen and final cage closing of C_{60}.[1, 2] It is a point of interest whether hydrogen acceptors can be used to stabilise endohedral hydrogen in other molecular states than as a diatomic homonuclear molecule. The arc discharge method in a reactive gas atmosphere[3] has proven to be an efficient method for producing new endohedral cluster fullerenes with high yield and selectivity. This has been shown for the two isomers of $Sc_3N@C_{80}$ as well as for the $Tm_3N@C_{2n}$ ($39 \leq 2n \leq 43$) and $Dy_3N@C_{2n}$ ($39 \leq 2n \leq 44$) families.[4–6]

Herein, a route to encapsulate chemically bonded hydrogen in a fullerene is reported. This entrapment is reached by a one-stage process using an arc burning in a reactive CH_4 atmosphere caging a Sc_3CH cluster in C_{80}. The isolated endohedral fullerene $Sc_3CH@C_{80}$ was characterised by high-resolution mass spectrometry, electron spin resonance, UV/Vis-NIR, ⁴⁵Sc NMR and Raman spectroscopy. Density functional theory (DFT) calculations were employed to confirm the proposed structure, elucidate further structural details and to compare relative stabilities of alternative geometric configurations.

Results and Discussion

The chromatographic analysis of fullerene soot produced by arc burning of scandium in a reactive methane/helium atmosphere revealed a fullerene structure with an integer mass-to-charge ratio of $m/q = 1108$, which none of the possible structures of the elements carbon and scandium could account for.

In high-pressure liquid chromatography (HPLC) separation, this fullerene structure was found in the fraction of empty C_{86}. The retention time of the new fullerene structure was 81 min. This value is slightly shorter than the retention time of the nitride cluster fullerene $Sc_3N@C_{80}$, which was eluted after 84 min, and slightly longer than that of $Sc_3N@C_{78}$ (78 min).

The new fullerene structure was isolated by a multistage HPLC protocol and analysed at first by standard and high-resolution laser desorption time-of-flight mass spectrometry (LD-TOF-MS). The stability throughout the chromatographic separation is an indication for the endohedral nature of the structure. The positive and negative ion mass spectra of the isolated fullerene, shown in Figures 1a and 1b, demonstrate the chemical identity and the purity of $\geq 92\%$. The precursor peak in the positive ion mass spectrum at $m/q = 1107$ indicates the presence of one hydrogen atom in the structure of the new fullerene, which can be split off.

The accurate mass-to-charge ratio of the new fullerene was determined by the addition of an internal standard of empty fullerenes to the sample. The high-resolution LD-TOF mass spectrum (Figure 1c) confirms the molecular mass of the C_{92}

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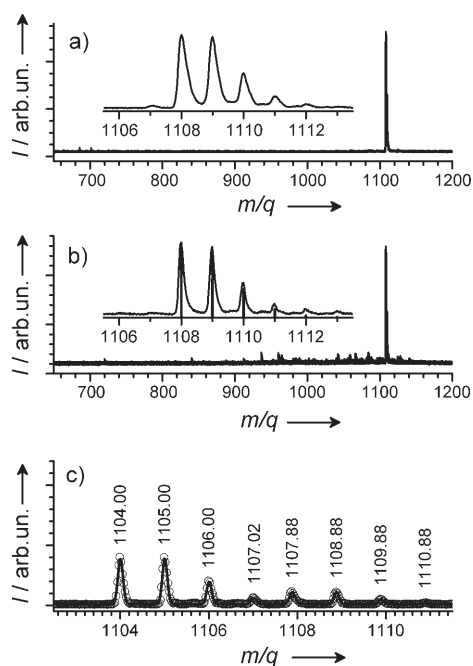**Figure 1.** a) Positive ion mass spectrum of $Sc_3CH@C_{80}$ with expanded molecular ion peak region as inset; b) Negative ion mass spectrum of $Sc_3CH@C_{80}$ with expanded molecular ion peak region and theoretical isotopic pattern (solid bars) as inset; c) Molecular ion peak region of a $Sc_3CH@C_{80}$ sample with an internal C_{92} standard measured with positive ion detection. Peak labels for both fullerenes are shown. All mass spectroscopic experiments were carried out without any matrix.

Figure 2. Vis-NIR (A) and ^{45}Sc NMR spectra (B) of $Sc_3CH@C_{80}$ (a) and $Sc_3N@C_{80}$ (I) (b). In part A, the structures have been dissolved in toluene. The insets show the HOMO–LUMO transition range. The lowest energetic absorptions of both endohedral fullerenes are marked by arrows. In part B, the samples were dissolved in carbon disulfide and acquisitions with 383 600 (a) and 180 000 (b) scans were made.

standard at 1104.00 g mol^{-1} and reveals a mass-to-charge number of 1107.88 for the new fullerene structure. An analysis of chemical structures covering the elements carbon, scandium, hydrogen, oxygen, and nitrogen lead to the conclusion that exclusively the chemical formula $C_{81}HSc_3$ can account for the observed mass-to-charge ratio with sufficient accuracy. Its theoretical molecular weight of 1107.876 g mol^{-1} is in full agreement with the experimental value of 1107.88 g mol^{-1}. Furthermore, the theoretical isotopic pattern of $C_{81}HSc_3$ is in very good agreement with the observed pattern (inset of Figure 1 b). The small intensity upset of the peak at $m/q = 1109$ and the weak peak at $m/q = 1113$ can be explained by a 5 % $Sc_3N@C_{80}$ contamination in the sample, which might be caused by a small amount of this structure residing in the production line from previous fullerene production series.

To detect whether an open or closed shell electronic configuration exists, the new fullerene was dissolved in toluene and studied by electron spin resonance (ESR) spectroscopy. Neither at room temperature nor at 4 K could any ESR signal attributable to the fullerene be detected. The isolated structure is diamagnetic; an unpaired electron in the structure can be ruled out.

UV/Vis-NIR, ^{45}Sc NMR and Raman spectroscopy were used for further structural characterisation of the isolated new fullerene. The Vis-NIR spectrum of the yellow solution in toluene has no absorption in the near-infrared range. The lowest energetic transition was found at 735 nm, corresponding to an optical HOMO–LUMO energy gap of 1.7 eV (Figure 2, part A). This
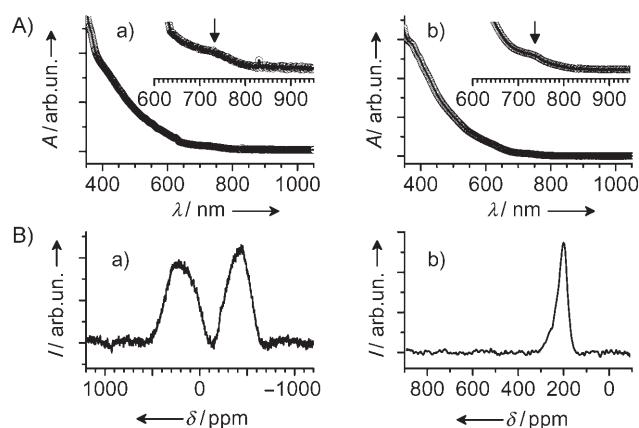
is exactly the same value which was formerly obtained for the $Sc_3N@C_{80}$ (I) isomer. For comparison, the lowest energetic transitions of $Sc_3N@C_{80}$ (II) and of $La_2@C_{80}$ were found at 780 nm and at 880 nm, respectively.[3,4] Thus, the new structure represents a large energy gap fullerene. Further absorptions were found at 445 and 555 nm.

To clarify the structure and chemical nature of the three scandium and one hydrogen atom, the ^{45}Sc NMR spectrum of the new fullerene structure with $m/q = 1108$ was compared with that of $Sc_3N@C_{80}$. Two equally intense NMR lines were observed in the spectrum of the new fullerene structure (Figure 2, part B). This doublet structure of the ^{45}Sc resonance is completely different from the singlet ^{45}Sc NMR signal of $Sc_3N@C_{80}$ (Figure 2, part B).[7] The existence of a cluster consisting of three equivalent scandium atoms which interact with one atom of nuclear spin of $^1/_2$ is thus demonstrated. The only possibility consistent with this conclusion is that the ^{45}Sc NMR doublet is the result of magnetic coupling between the scandium nuclear spin and that of hydrogen. The three scandium atoms and the hydrogen are therefore bonded within one chemical moiety, a Sc_3CH cluster. The nuclear spins couple over two bonds, one Sc–C and one Sc–H bond. This finding proves the chemical nature of the new fullerene structure. It consists of a Sc_3CH cluster and a C_{80} fullerene cage. By comparing the shift of $Sc_3CH@C_{80}$ with that of $Sc_3N@C_{80}$, any interference of a $Sc_3N@C_{80}$ impurity in the NMR spectrum is avoided.

The low-energy Raman spectra of $Sc_3CH@C_{80}$ show the well-known vibrational structure of fullerene cages (Figure 3, Table 1, and Supporting Information). The line at 486 cm^{-1} and the line groups at around 374 cm^{-1} and 235 cm^{-1} are correlated with the $A_g(1)$, $H_g(2)$ and $H_g(1)$-derived cage modes in $Sc_3N@C_{80}$ (I) and $La_2@C_{80}$ and provide spectroscopic evidence for the presence of the same C_{80} cage.[8,9] The strong line at 211 cm^{-1} has a counterpart only in the spectra of the $Sc_3N@C_{80}$ isomers. Since this line was assigned to a Sc_3N translation mode for $Sc_3N@C_{80}$,[10] its observation in the $Sc_3CH@C_{80}$ spec-
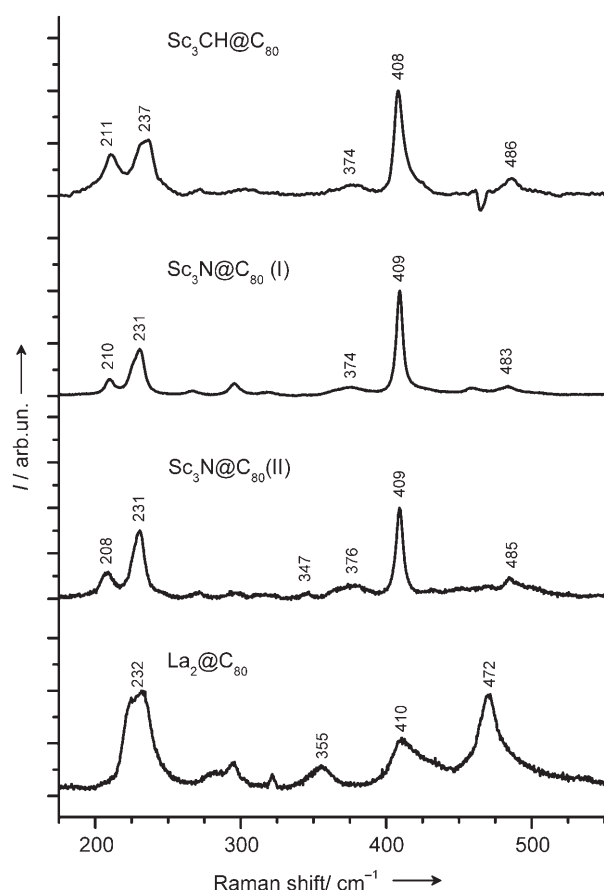
Figure 3. Normalised Raman spectra of Sc₃CH@C₈₀, Sc₃N@C₈₀ (I), Sc₃N@C₈₀ (II), and La₂@C₈₀ (from top to bottom). Laser wavelength 647 nm, laser power 20 mW, accumulation time 12 h. Spectra were baseline corrected and shifted along the y-axis for presentation.

Table 1. Wave numbers (cm⁻¹), relative intensities, and assignment for low-energy Raman modes of Sc₃CH@C₈₀, Sc₃N@C₈₀ (I), Sc₃N@C₈₀ (II), La₂@C₈₀. The abbreviations for the relative intensities have the usual meaning.

Sc₃CH@C₈₀	Sc₃N@C₈₀ (I)[8]	Sc₃N@C₈₀ (II)	La₂@C₈₀	Assignment[8,9]
211 s	210 vs	208 m	–	δ(ScRSc), R=N, CH
231 vs	226 sh	227 sh	220 s	H_g(1)
237 vs	231 vs	231 vs	232 s	H_g(1)
364 w	365 w	366 w	348 w	H_g(2)
374 w	374 w	376 w	355 m	H_g(2)
382 w	382 w	383 w	361 w	H_g(2)
408 vs	409 vs	409 vs	410 w–m	{ν(Sc₃R), R=N, CH + ν(cage)}, ν(cage) in La₂@C₈₀
486 m	483 m	485 w–m	471 s	A_g(1)

derived squashing mode. The larger the deviation from an ideal sphere, the larger the splitting of this lowest energetic fullerene cage line. This was demonstrated for the isomers of empty C₇₈, C₈₀, C₈₂ and C₈₄, where the splitting was 15 cm⁻¹ for the most uniformly shaped C₈₄:23 (D_{2d}) isomer and approached 50 cm⁻¹ for ellipsoidal shaped cages such as D_2 C₈₀ and D_3 C₇₈.[11, 12] The H_g(1)-derived modes of Sc₃CH@C₈₀ appeared at 231 and 237 cm⁻¹. This is at 4.5 and 6.0 cm⁻¹ higher wave numbers than in Sc₃N@C₈₀ (I). The splitting in Sc₃CH@C₈₀ is 6 cm⁻¹, very close to the values in the Sc₃N@C₈₀ isomers (Table 1), and much smaller than in the empty cages[11] and in La₂@C₈₀ (Figure 3 and Table 1). Such a small splitting is structural evidence for a spherical carbon cage, whose symmetry is only slightly distorted. Therefore, the Raman spectra show the following two structural properties of the new fullerene Sc₃CH@C₈₀: a spherical C₈₀ cage and a Sc₃CH cluster inside. An exohedral bonding of Sc₃CH would distort the spherical structure of the fullerene cage. Then, the HPLC retention times would have been extended and the line splitting of the H_g(1) squashing mode would be significantly larger. Due to the HPLC retention time and the Vis-NIR and the Raman spectra, Sc₃CH@C₈₀ is assigned to the C₈₀:7 (I_h) cage isomer. In summary, the experimental characterisation provided extensive and consistent evidence for the first isolation of an endohedral Sc₃CH@C₈₀ fullerene.

By DFT calculations, a further structural description of the endohedral situation of the new cluster can be presented. Thus geometry optimisation of C_3 Sc₃CH@C₈₀ results in a structure very similar to that of Sc₃N@C₈₀. The cluster, which is slightly pyramidal (with pyramid height 0.25 Å), has Sc—C(H) bonds somewhat longer than Sc—N bonds in a nitride cluster (2.109 versus 2.034 Å), while the shortest Sc—C(cage) bonds are somewhat shorter than in Sc₃N@C₈₀ (2.241 versus 2.263 Å). The rotation angle of the cluster around the C_3 axis and the geometric parameters of Sc₃CH@C₈₀ and Sc₃N@C₈₀ are slightly different (18.6° for Sc₃CH and 22.1° for Sc₃N with respect to the C_{3v} symmetric configuration). For comparison, the geometric and energetic properties of the most likely structures of an endohedral Sc₃C cluster and an exohedrally bonded hydrogen to the C₈₀ cage with the chemical formula Sc₃C@C₈₀H were also calculated. If C_3 symmetry is proposed for Sc₃C@C₈₀, formally there are 28 symmetry non-equivalent addition sites for the hydrogen atom. For energetic reasons, only 20 addition sites have to be considered, and 20 isomers of Sc₃C@C₈₀H were optimised at DFT level (see supporting information for details). The relative energies and HOMO–LUMO gaps of all computed structures result in two important facts: a) even the most stable structure of Sc₃C@C₈₀H is 94 kJ mol⁻¹ less stable than Sc₃CH@C₈₀; b) the HOMO–LUMO gaps of the Sc₃C@C₈₀H isomers are at least 0.2 V smaller than the gap in Sc₃CH@C₈₀. It should be pointed out that the gap in Sc₃CH@C₈₀ is very close to the predicted gap in Sc₃N@C₈₀, which is in good agreement with very similar absorption patterns for these two compounds. Therefore, both the relative energy and the HOMO–LUMO gap clearly favour the endohedral Sc₃CH@C₈₀ structure as illustrated in Figure 4.
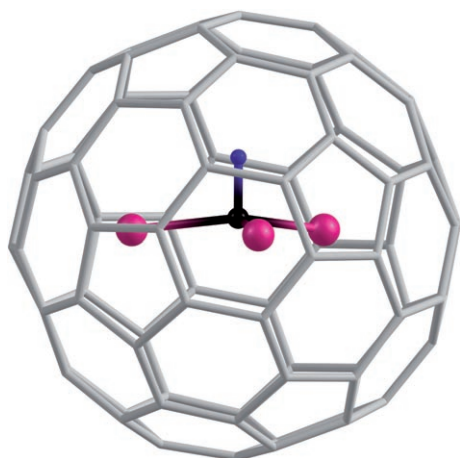
trum is a fingerprint of a similar constituent, that is, a cluster of the composition Sc₃CH. Moreover, the dominating Raman line at 408 or 409 cm⁻¹ is characteristic for C₈₀ structures with an encaged Sc₃X (X=N, CH) cluster.

An independent spectroscopic measure for the geometry of a fullerene cage is given by the splitting energy of the H_g(1)-

Figure 4. Calculated structure of $Sc_3CH@C_{80}$. Gray: C_{80} cage atoms; black: carbon atom of the Sc_3CH cluster; pink: scandium atoms; blue: hydrogen atom.

Conclusions

In summary, the concept of a reactive gas atmosphere proves to be a general method for the generation of new cluster fullerenes differing in their cluster composition and cluster atom number from those known to date. Here for the first time a hydrocarbon is stabilised inside a fullerene in the chemical form of a five-atom Sc_3CH cluster. As hydrogen is stabilised in the covalent cluster Sc_3CH inside the C_{80} cage, this procedure opens a new route for a well-defined type of hydrogen encapsulation in carbon nanostructures, completely different from the molecular hydrogen in C_{60}.

Experimental Section

Fullerenes were produced by the Krätschmer–Hufman arc burning method with an atmosphere of 20 mbar methane and 200 mbar helium. Mixtures of scandium powder and graphite powder were pressed into the 6 mm wide holes of graphite rod electrodes in a molar metal/carbon ratio of 1:12.5. For one burning process, 5 g of initial material were used. This procedure was repeated 20 times. The fullerene soot was purified with acetone and subsequently Soxhlet extracted by CS_2 for 20 h. Fullerene separation was done by multistage HPLC with toluene as the eluent. $Sc_3CH@C_{80}$ was isolated from the C_{86} fraction in three steps using a combination of two analytical 4.6×250 mm BuckyPrep columns (Nacalai Tesque). Herein, 25 µg $Sc_3CH@C_{80}$ were isolated with a chromatographic and mass spectroscopic purity of 92%. The mass spectrometric analysis was performed by the laser desorption time-of-flight (LD-TOF) method running both in positive and negative ion modes (Biflex III, Bruker, Germany). The accuracy of the m/q values is better than 0.02 using a reference. ^{45}Sc NMR spectroscopy was performed at 121.5 MHz in a multiprobe head PH 1152Z of an Avance 500 spectrometer (Bruker) at room temperature in carbon disulfide solutions with $[D_6]$acetone as a lock and a 0.2 M $Sc(NO_3)_3$ solution

in concentrated HNO_3 as a reference. Electron spin resonance of $Sc_3CH@C_{80}$ dissolved in toluene was measured with an EMX X-Band continuous-wave (cw) ESR Spectrometer (Bruker) at 100 kHz modulation between room temperature and 4 K. The solution was degassed and sealed in a quartz tube of 4 mm diameter under high vacuum. The Vis-NIR spectrum of a $Sc_3CH@C_{80}$ solution in toluene was recorded on an UV/Vis-NIR 3101-PC spectrometer (Shimadzu, Japan). For Raman measurements, $Sc_3CH@C_{80}$ was dissolved in toluene and drop coated on a KBr single crystal disk. The films were dried in air and mounted on a sample rotation device. Room temperature Raman spectra of the rotating sample were measured with a T 64000 triple spectrometer (Jobin Yvon, France) using visible laser radiation at 515 nm and 647 nm for excitation (Innova 300 series, Coherent, USA).

DFT computations were performed with the PRIRODA package[13] employing PBE density functional[14] and implemented TZ2P-quality basis set with effective-core potential for Sc atoms.

[1] Y. Murata, M. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2003**, *125*, 7152–7153.
[2] K. Komatsu, M. Murata, Y. Murata, *Science* **2005**, *307*, 238–240.
[3] L. Dunsch, M. Krause, J. Noack, P. Georgi, *J. Phys. Chem. Solids* **2004**, *65*, 309–315.
[4] M. Krause, L. Dunsch, *ChemPhysChem* **2004**, *5*, 1445–1449.
[5] M. Krause, J. Wong, L. Dunsch, *Chem. Eur. J.* **2005**, *11*, 706–711.
[6] S. Yang, L. Dunsch, *J. Phys. Chem. B.* **2005**, 109, 12320–12328.
[7] For a comparison of the Sc shift in different chemical structures see: B. Gierczyk, G. Schroeder, *Pol. J. Chem.* **2003**, *77*, 1741–1745.
[8] M. Krause, H. Kuzmany, P. Georgi, L. Dunsch, K. Vietze, G. Seifert, *J. Chem. Phys.* **2001**, *115*, 6596–6605.
[9] H. Shimotani, T. Ito, Y. Iwasa, A. Taninaka, H. Shinohara, E. Nishibori, M. Takata, M. Sakata, *J. Am. Chem. Soc.* **2004**, *126*, 364–369.
[10] S. Yang, S. I. Troyanov, A. A. Popov, M. Krause, L. Dunsch, *J. Am. Chem. Soc.* **2006**, *128*, 16733–16739.
[11] H. J. Eisler, S. Gilb, F. Hennrich, M. M. Kappes, *J. Phys. Chem.* A **2000**, *104*, 1769–1774.
[12] M. Krause, M. Hulman, H. Kuzmany, M. Inakuma, H. Shinohara, *J. Chem. Phys.* **1999**, *111*, 7976–7984.
[13] D. N. Laikov, *Chem. Phys. Lett.* **1997**, *281*, 151–156.
[14] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.