^{13}C NMR spectroscopic study of scandium dimetallofullerene, $Sc_2@C_{84}$ *vs.* $Sc_2C_2@C_{82}$

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Although Sc_2C_{84} has been widely believed to have the form $Sc_2@C_{84}$, the present ^{13}C NMR study reveals that it is a scandium carbide metallofullerene, $Sc_2C_2@C_{82}$, which has a $C_{82}(C_{3v})$ cage.

Endohedral metallofullerenes have attracted special attention as new spherical molecules with unique properties, unexpected of 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 metallofullerenes are of special interest because of the high variety of fullerene sizes, as well as their relatively high yields.[4] In this context, it is a very important challenge to determine the structures of typical scandium metallofullerenes. For Sc_2C_{84}, three isomers (I, II and III) have been isolated up to now. These isomers have been investigated and discussed by XPS,[5] ^{13}C NMR,[6,7] ^{45}Sc NMR,[8] IR[9] and Raman[10] spectroscopic measurements, powder X-ray analysis,[11] and theoretical calculations,[12] on the premise that the two Sc atoms are encapsulated inside the C_{84} fullerene. For C_{84}, there are 24 cage isomers that satisfy the so-called isolated pentagon rule (IPR).[13] The ^{13}C NMR measurement of the most abundant isomer of Sc_2C_{84}(III) have indicated that the two Sc atoms are encapsulated inside the D_{2d} cage isomer of C_{84}. This structure, $Sc_2@C_{84}$, has also been confirmed by the maximum entropy method (MEM)/Rietveld analysis of synchrotron X-ray powder diffraction data.[11] We herein report the ^{13}C NMR re-investigation of Sc_2C_{84}(III).

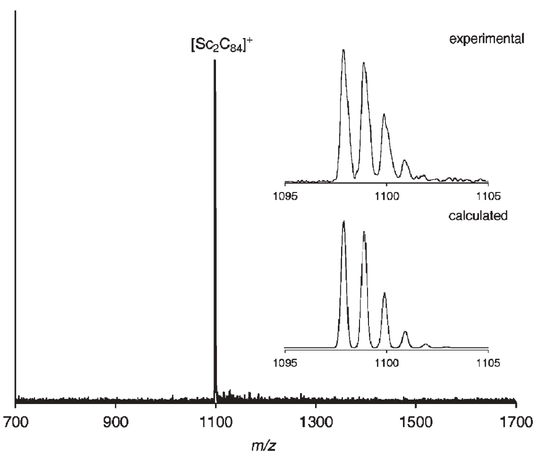

Fig. 1 The LD-TOF mass spectrum of Sc_2C_{84}.

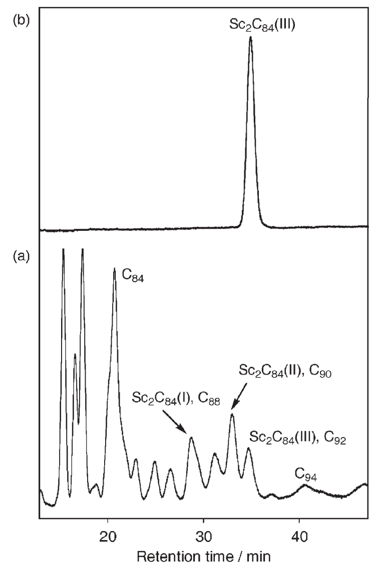

Fig. 2 The HPLC profiles of (a) extract and (b) isolated Sc_2C_{84} by a Buckyprep column (ϕ4.6 × 250 mm, 1.0 mL min^{-1} flow rate, toluene eluent).

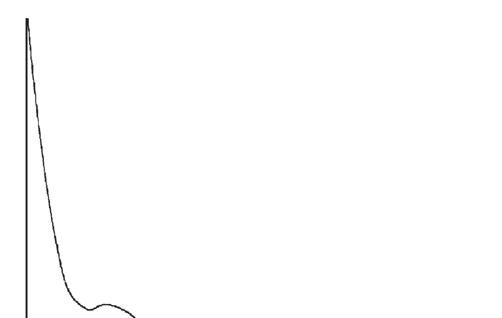

Fig. 3 The visible-NIR absorption spectrum of Sc_2C_{84} in CS_2.

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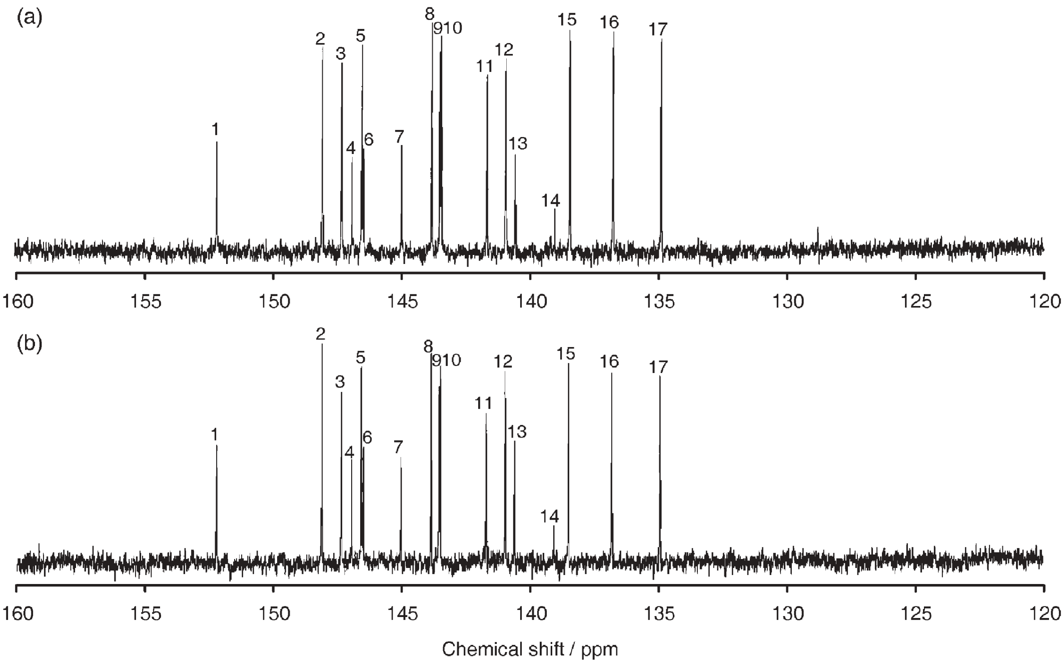

Fig. 4 The ^{13}C NMR spectra (125 MHz, CS_2) of Sc_2C_{84} in (a) proton-decoupled mode and (b) proton-coupled mode at 298 K. A capillary containing acetone-d_6 was used as an internal lock.

The soot containing scandium metallofullerenes was prepared according to the reported procedure.[4] The Sc/C composite rod (4.7 × 10 × 150 mm, 2.0 atom%) was arc-vaporized at 150 A and 40 V under helium at 50 Torr. The raw soot was collected and extracted with 1,2,4-trichlorobenzene (TCB) for 15 hours. Sc_2C_{84}(III)[14] was separated and isolated in *ca.* 2% yield from various empty fullerenes and other scandium metallofullerenes by a multi-stage HPLC method.[6] As shown in Fig. 1 and Fig. 2, the HPLC and LD-TOF mass analysis confirm that the isolated Sc_2C_{84}(III) sample contains neither empty fullerenes nor other metallofullerenes. The visible-NIR spectrum of the isolated Sc_2C_{84}(III) is shown in Fig. 3.

In the previous ^{13}C NMR study of Sc_2C_{84}(III), only 11 lines (10 lines of nearly equal intensity and one line of half intensity) were observed.[6] On the basis of this observation, it was concluded that the two Sc atoms are equivalently encapsulated inside the D_{2d} cage of C_{84} along the C_2 axis. However, we have been able to obtain an improved ^{13}C NMR spectrum of Sc_2C_{84}(III) in carbon disulfide (CS_2) at 298 K, which has much smaller signal-to-noise ratio across a wider range (120–160 ppm) than the previous system (132–150 ppm). As clearly shown in Fig. 3, we have observed a total of 17 lines (11 full-intensity lines, 5 half-intensity lines and one ⅙-intensity line)[15] Obviously, this ^{13}C NMR pattern is not satisfied by placing the two Sc atoms inside any of the IPR-satisfying C_{84} cage isomers. It is interesting that the ^{13}C NMR pattern can be well explained by the fact that the carbon cage of Sc_2C_{84}(III) originates from the C_{3v}(8) isomer of C_{82},[16] and two C atoms as well as two Sc atoms are encapsulated inside the C_{82} fullerene.[17] This endohedral structure, $Sc_2C_2@C_{82}$, disagrees with the $Sc_2@C_{84}$ structure determined by the powder X-ray MEM/Rietveld analysis.[11]† However, it is noteworthy that the visible-NIR (Fig. 3) and ^{13}C NMR (Fig. 4) spectra are very similar to those observed for $Y_2C_2@C_{82}$(III), in which Y_2C_2 is supposed to be encapsulated inside the C_{3v}(8) isomer of C_{82}.[18,19]

In conclusion, the present ^{13}C NMR study shows that the structure of Sc_2C_{84}(III) is not $Sc_2@C_{84}$ but $Sc_2C_2@C_{82}$.

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Notes and references

† The same has been also found for the case of Sc_3C_{82}. Although the structure of $Sc_3@C_{82}$ has been determined by powder X-ray MEM/Rietveld analysis,[20a] the recent ^{13}C NMR and X-ray single crystal structure analyses show that Sc_3C_{82} takes the form of $Sc_3C_2@C_{80}$.[20b]

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