

¹³C-NMR Study on the Structure of Isolated Sc₂@C₈₄ Metallofullerene

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Endohedral metallofullerenes have gained extremely wide interest in recent years because of their novel structural and electronic properties.^{1,2} Most of the monometallofullerenes prepared so far have been based on C₈₂ and have incorporated lanthanum,^{1,3–5} yttrium,^{6,7} scandium,^{8–10} and most of the lanthanide elements.^{11,12} Very recently, the endohedral nature of Y@C₈₂ has been finally confirmed by a synchrotron X-ray powder diffraction study.¹³ However, to date no structural model has been derived experimentally for the endohedral nature of dimetallofullerenes such as Sc₂@C₈₄^{8,10,14–16} and La₂@C₈₀,^{3,17,18} although an endohedral nature of Sc₂@C₈₄ has been strongly suggested by previous scanning tunneling microscopy¹⁵ and transmission electron microscopy¹⁶ studies. Here we report the first ¹³C-NMR results on the metallofullerene, Sc₂@C₈₄, which determines an isomer cage structure for the metallofullerene.

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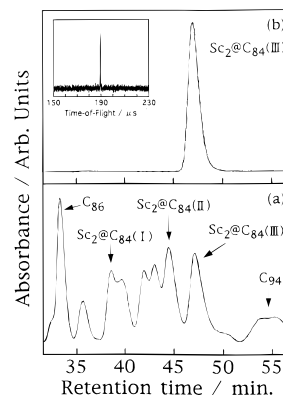
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Figure 1. HPLC chromatograms of (a) the first and (b) the third (isolation) stages for the separation of Sc₂@C₈₄(III). In the first HPLC stage (a), the HPLC peaks of isomers I, II, and III are overlapped with those of hollow C₈₈, C₉₀, and C₉₂ fullerenes, respectively (see text).

The details of the production and separation/isolation of endohedral scandium metallofullerenes have been described elsewhere.^{14,19–21} Briefly, soot containing Sc₂@C₈₄ and other scandium metallofullerenes was produced in direct-current (500 A) spark mode under He flow at 50 Torr and collected under totally anaerobic conditions.^{14,20,21} Even under these anaerobic conditions, Sc@C₆₀ and Sc@C₇₀ were not extracted by solvents. The Sc₂@C₈₄ fullerene was separated and isolated from the various hollow fullerenes (C₆₀–C₁₁₀) and other scandium metallofullerenes by the multistage high-performance liquid chromatography (HPLC) method^{14,20} by using two complementary types of HPLC columns.²² The purity of Sc₂@C₈₄ relative to other fullerenes was more than 99.9%. ¹³C-NMR measurements were made using a 600 MHz NMR (JEOL JNM-A600) at room temperature in CS₂ solvent.

Panels a and b of Figure 1 show the HPLC chromatograms for the first and final (third) HPLC stages for the separation of Sc₂@C₈₄, respectively. As seen in Figure 1a, there are at least three HPLC peaks that correspond to different structural isomers of Sc₂@C₈₄. Hereafter, we call these isomers I, II, and III of Sc₂@C₈₄ in increasing order of retention time (cf. Figure 1a).²³ It was found that the retention times of isomers I, II, and III coincide with those of hollow C₈₈, C₉₀, and C₉₂ fullerenes, respectively, under the present HPLC conditions.²² The complete separation of these isomers was achieved, however, in the final HPLC stage.²⁴ Figure 1b shows the final HPLC (i.e., isolation) stage for isomer III which is the most abundant isomer of Sc₂@C₈₄.

A ¹³C-NMR spectrum of Sc₂@C₈₄(III) in CS₂ solution is shown in Figure 2. The spectrum was obtained after 130 000 scans (for 144.5 h) at room temperature. The spectrum consists of a series of 10 distinct lines of near-equal intensity and one

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(24) In the three-stage separation, isomers I and II were also isolated as well as isomer III.

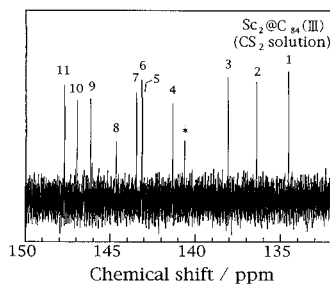


Figure 2. ^{13}C -NMR spectrum of $\text{Sc}_2@C_{84}(\text{III})$ in CS_2 [added $\text{Cr}(\text{acac})_3$ (acac, acetylacetonate) as a relaxant] after 130 000 scans at room temperature. The marked peak is due to impurities.

additional line at half the intensity.²⁵ All of the 11 NMR signals appear in the chemical shift range 134–148 ppm, which is similar to that of hollow C_{84} (134–145 ppm). A wider range spectrum (not shown) shows no other resonances, confirming high sample purity.

It is well-known that there are 24 IPR (isolated pentagon rule)²⁶ satisfying structural isomers for the hollow C_{84} fullerene.²⁷ Experimentally, two isomers, D_2 (No. 22)²⁷ and D_{2d} (No. 23),²⁷ are mainly produced by arc discharge of graphite rods.²⁸ The result that the present NMR spectrum shows 10 strong lines of near-equal intensity and a weak line at half the intensity is compelling evidence²⁷ that the $\text{Sc}_2@C_{84}(\text{III})$ metallofullerene has the D_{2d} (No. 23) symmetry and that the two scandium atoms must be equivalent within the time scale of the NMR measurements. This reflects the geometrical equivalence of the two Sc atoms in the C_{84} cage. The present NMR results show that the two Sc atoms are indeed trapped within the C_{84} cage. A similar equivalence of trapped atoms has been reported on an endohedral triscandium fullerene, $\text{Sc}_3@C_{82}$, based on an analysis of the hyperfine structure of the corresponding ESR measurements.^{8,10,20}

An endohedral structural model for $\text{Sc}_2@C_{84}(\text{III})$, which is consistent with the present ^{13}C -NMR result, is presented in Figure 3; the two Sc atoms are engaged along the D_{2d} axis of

(25) Observed line positions (ppm) (and relative intensities): 134.57 (2.3), 136.44 (2.1), 138.11 (2.2), 141.36 (1.7), 143.14 (1.7), 143.18 (2.1), 143.49 (1.8), 144.67 (1.0), 146.19 (1.7), 146.99 (1.7), 147.73 (1.9).

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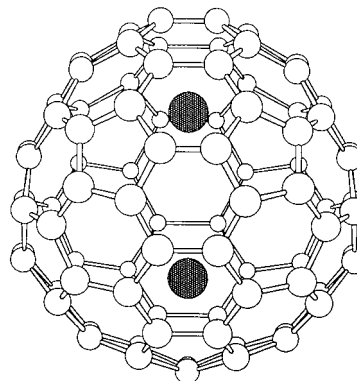


Figure 3. Static molecular structure for $\text{Sc}_2@C_{84}(\text{III})$ consistent with the ^{13}C -NMR results (see text).

the $C_{84}-D_{2d}$ (No. 23) fullerene in a symmetric position with respect to the center of the C_{84} cage. A recent *ab initio* calculation²⁹ has predicted that such an endohedral structure is the most stable structure. It also predicts that each Sc atom donates two valence electrons to the C_{84} cage, leading to a formal electronic structure $(\text{Sc}^{2+})_2@C_{84}^{4-}$. However, at least at room temperature, some dynamical averaging of the Sc ions might be taking place around the optimum scandium position such as in Figure 3. This is mainly due to Coulomb repulsion between the two Sc^{2+} cations within the cage. This dynamical picture for the endohedral structure of $\text{Sc}_2@C_{84}(\text{III})$ is also consistent with the present NMR results. In fact, our preliminary synchrotron X-ray powder diffraction study on $\text{Sc}_2@C_{84}(\text{III})$ ³⁰ shows strong evidence that this is a better structural description than the static picture.

The fact that in $\text{Sc}_2@C_{84}$ the two Sc atoms are preferentially trapped within one of the two major isomers of the corresponding hollow C_{84} fullerene, $C_{84}-D_{2d}$ (No. 23), will be an important clue for elucidating the growth mechanism of endohedral metallofullerenes. ^{13}C -NMR studies on the other two isomers, $\text{Sc}_2@C_{84}(\text{I})$ and $\text{Sc}_2@C_{84}(\text{II})$, are now in progress.

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