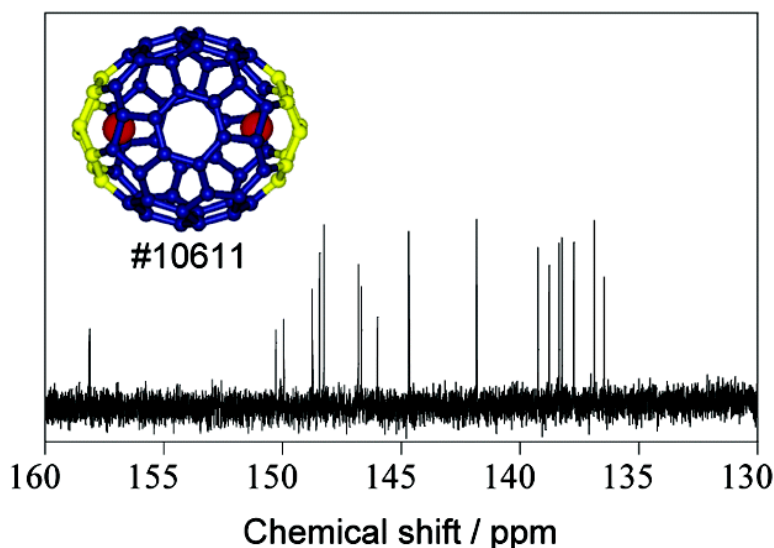


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## Structure of a Missing-Caged Metallofullerene: $\text{La}_2@C_{72}$

Haruhito Kato,<sup>†</sup> Atsushi Taninaka,<sup>†</sup> Toshiki Sugai,<sup>†</sup> and Hisanori Shinohara<sup>\*†‡</sup>

Department of Chemistry and Institute for Advanced Research, Nagoya University, Nagoya, 464-8602, Japan, and  
CREST, Japan Science Technology Corporation, c/o Department of Chemistry, Nagoya University,  
Nagoya 464-8602, Japan

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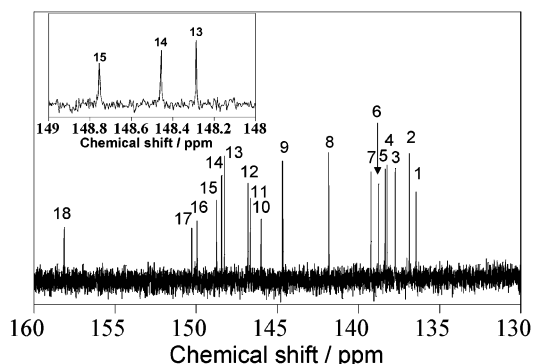
Endohedral metallofullerenes<sup>1</sup> have attracted much attention during the past decade not only for their structural/electronic novelty but for promising biomedical applications such as MRI contrast agents.<sup>2–4</sup> Recently, it has been demonstrated that otherwise unstable species such as metal clusters,<sup>5</sup> carbides,<sup>6</sup> and nitrides<sup>7</sup> can safely be entrapped in several fullerene cages. This shows that the endohedral hollow space of fullerenes can provide a unique nanometer-scale field for stabilizing unstable species. Furthermore, even fullerene cages which do not obey the isolated-pentagon rule (IPR)<sup>8</sup> having “fused-pentagon” can well be stabilized by encapsulation of metal atoms, that is,  $\text{Sc}_2@C_{66}$ <sup>9</sup> and  $\text{Sc}_3\text{N}@C_{68}$ .<sup>10</sup>

In contrast,  $C_{72}$  and  $C_{74}$  fullerenes (the so-called “missing fullerenes”<sup>11</sup>), which have never been isolated due to their structural instability even though they have  $D_{6d}$  and  $D_{3h}$  IPR structures, respectively, are much stabilized and even isolated only when they form metallofullerenes such as  $M_n@C_{72}$  ( $n = 0$ ,<sup>12</sup>  $n = 1$  for  $M = \text{Ca}$ ,<sup>11</sup>  $n = 2$  for  $M = \text{Sc}$ ,<sup>13</sup>  $\text{La}$ ,<sup>14</sup> and  $\text{Ce}$ <sup>15</sup>) and  $M_n@C_{74}$  ( $n = 0$ ,<sup>16</sup>  $n = 1$  for  $\text{Ca}$ ,<sup>11,17</sup>  $\text{Sm}$ ,<sup>18</sup> and  $\text{Eu}$ ,<sup>17,19</sup>  $n = 2$  for  $\text{Sc}$ <sup>20</sup>). However, the structures of  $M_n@C_{72}$  and  $M_n@C_{74}$  fullerenes have not been elucidated yet. Here, we present the first structural analysis of the  $C_{72}$  fullerene encapsulating two La atoms, that is,  $\text{La}_2@C_{72}$ , by high-resolution <sup>13</sup>C NMR.

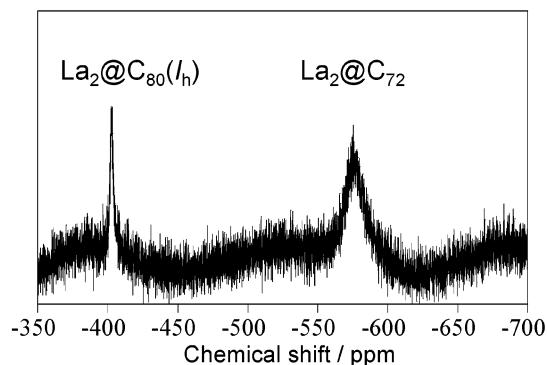
Details of the synthesis and isolation of metallofullerenes were described elsewhere.<sup>1</sup> Briefly, soot containing  $\text{La}_2@C_{72}$  and other La-fullerenes were produced by DC arc discharge (500 A, 20 V) of La/graphite composite rods (15 × 15 × 300 mm, 1.6 at. % of La, Toyo Tanso Co.) under He flow (15 L/min) conditions. The isolation of  $\text{La}_2@C_{72}$  was achieved by the two-stage HPLC method.<sup>1,14</sup> The purity of  $\text{La}_2@C_{72}$  was >99%, as was revealed by both laser-desorption TOF mass spectrometry and HPLC analyses.  $\text{La}_2@C_{72}$  is fairly stable under ambient conditions. This suggests that the HOMO–LUMO gap of  $\text{La}_2@C_{72}$  is large, which is consistent with the onset of UV–vis–NIR absorption spectra<sup>15</sup> previously reported.

The <sup>13</sup>C NMR spectrum of  $\text{La}_2@C_{72}$  in  $\text{CS}_2$  solution presents 18 lines in a diamagnetic chemical shift range from 130 to 160 ppm (cf., Figure 1). The intensities of line numbers 10 (146.0 ppm), 15 (148.7 ppm), 16 (150.0 ppm), 17 (150.3 ppm), and 18 (158.1 ppm) are smaller than those of other lines. The line widths of these lines are, however, larger than the others (cf., Figure 1, insert), indicating the presence of 18 lines of equal intensity. Transverse relaxation times ( $T_2$ ) of these lines could be faster than those of the other lines presumably because of somewhat localized electron transfers from La atoms to the  $C_{72}$  cage and/or of additional interactions other than the charge transfer.<sup>9</sup>

A <sup>139</sup>La NMR spectrum of a mixture of  $\text{La}_2@C_{72}$  and  $\text{La}_2@C_{80}$  ( $I_h$ ) (at 333.6 K and calibrated from <sup>1</sup>H NMR spectra of ethylene



**Figure 1.** <sup>13</sup>C NMR spectrum of  $\text{La}_2@C_{72}$  in  $\text{CS}_2$  (2.0 mg of  $\text{Cr}(\text{acac})_3$  as relaxant,  $\text{CDCl}_3$  lock) with 58 550 scans at room temperature using a JEOL Alpha spectrometer at 150 MHz. The <sup>13</sup>C NMR spectroscopic line position was referenced with respect to that of  $\text{CS}_2$  at 192.3 ppm.



**Figure 2.** <sup>139</sup>La NMR spectrum of a mixture of  $\text{La}_2@C_{72}$  and  $\text{La}_2@C_{80}$  ( $I_h$ ) in *o*-dichlorobenzene- $d_4$  with 200 704 scans at 333.6 K using a JEOL Alpha spectrometer at 84.65 MHz.

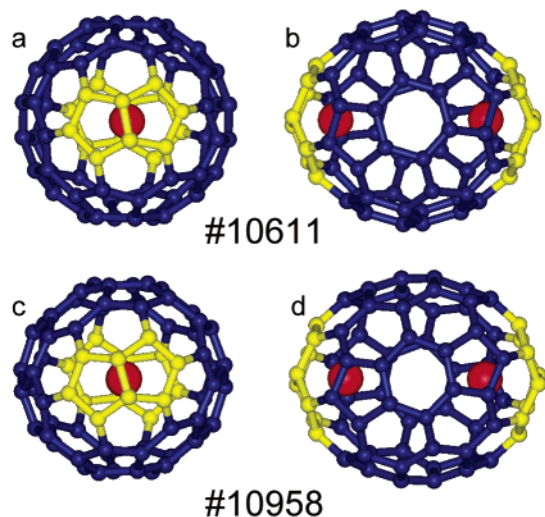
glycol<sup>21</sup>) is shown in Figure 2. The line position of <sup>139</sup>La NMR was calibrated with respect to that of  $\text{La}_2@C_{80}$  at  $-402.6$  ppm.<sup>22</sup> A single broad signal of  $\text{La}_2@C_{72}$  was observed at  $-575.6$  ppm, indicating that the two La atoms are geometrically equivalent inside the  $C_{72}$  cage. The broader <sup>139</sup>La NMR line width of  $\text{La}_2@C_{72}$  than that of  $\text{La}@C_{82}$  may indicate that  $\text{La}_2@C_{72}$  has lower symmetry and that transverse relaxation times ( $T_2$ ) of the <sup>139</sup>La nuclear spin of  $\text{La}_2@C_{72}$  are faster than those of  $\text{La}_2@C_{80}$  ( $I_h$ ).

The observed <sup>13</sup>C NMR spectrum pattern of  $\text{La}_2@C_{72}$  does not correspond to that of the only IPR structure of  $C_{72}$  with  $D_{6d}$  symmetry. The cage structure of  $\text{La}_2@C_{72}$  does not satisfy IPR.

Although there are a number of ways to violate IPR, the most straightforward way to do this is to generate the so-called “fused-pentagon”<sup>9</sup> where pentagons are adjacent with each other. The (very low field) NMR peak at 158.1 ppm suggests the presence of fused-pentagons.<sup>9,10,20</sup> For 72-atom carbon cages with hexagonal and pentagonal faces, there are in total 11 189 possible (non-IPR) structural isomers.<sup>23</sup> Considering the observed 18-lines, 24 structural

<sup>†</sup> Department of Chemistry and Institute for Advanced Research, Nagoya University.

<sup>‡</sup> CREST, Nagoya University.



**Figure 3.** Structures of proposed #10611 and #10958 for  $\text{La}_2@C_{72}$ , showing top views (left, a and c) and side views (right, b and d).

isomers of  $C_{72}$  with  $D_2$  symmetry can satisfy the observed  $^{13}\text{C}$  NMR pattern. Furthermore, when only the least number of fused-pentagons (i.e., two two-fused pentagons) is employed for  $C_{72}$  as in the case of  $\text{Sc}_2@C_{66}$ ,<sup>9</sup> only two such non-IPR structures are possible, that is, #10611 and #10958 (see Figure 3).

As was experimentally shown in the  $\text{Sc}_2@C_{66}$  case, in  $\text{La}_2@C_{72}$  we think also that each of the two two-fused pentagons can be stabilized by electron transfers from encaged La atoms and other interactions which are adjacent to these fused-pentagons. The rest of the 22 non-IPR structures for  $C_{72}$  possess much strained structures such as four two-fused pentagons, six two-fused pentagons, two six-fused pentagons, and so on, which obviously have substantially lower stability than the two two-fused pentagons case.

In general, HOMO–LUMO gaps of fullerenes are consistent with the onset of UV–vis–NIR absorption spectra of the fullerenes. The HOMO–LUMO gaps of the two  $C_{72}$  structural candidates, structures #10611 and #10958, were estimated as  $C_{72}^{6-}$  (where 6 electrons are transferred from La atoms to the  $C_{72}$  cage<sup>14</sup>) at RHF/3-21G with use of the Gaussian 98 program basis set for carbon atoms. The calculated HOMO–LUMO gap of  $C_{72}$  (#10611) is 0.2001 hartree, which is much larger than that (0.1666 hartree) of  $C_{72}$  (#10958). Also, the stability of  $C_{72}$  (#10611) is much larger than that of  $C_{72}$  (#10958). We, therefore, suggest that  $\text{La}_2@C_{72}$  has the non-IPR  $D_2$ - $C_{72}$  (#10611) cage structure in which each La atom is situated close to one of the two-fused pentagons. Because this  $D_2$ - $C_{72}$  (#10611) structure has chiral isomers, further HPLC separation by using the chiral stationary phase<sup>24</sup> and asymmetric osmylation<sup>25</sup> may lead to isolation of enantiomers of  $\text{La}_2@C_{72}$ .

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**Supporting Information Available:** Mass, UV–vis–NIR absorption spectra,  $^{13}\text{C}$  NMR spectra ( $C_6D_6$  and *o*-dichlorobenzene- $d_4$  lock at room temperature and 333.6 K), and  $^{139}\text{La}$  NMR spectra (*o*-dichlorobenzene- $d_4$ ) of  $\text{La}_2@C_{72}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843.
- (2) Cagle, D. W.; Alford, J. M.; Tien, J.; Wilson, L. J. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1997; Vol. 4, p 361.
- (3) Mikawa, M.; Kato, H.; Okumura, M.; Narazaki, M.; Kanazawa, Y.; Miwa, N.; Shinohara, H. *Bioconjugate Chem.* **2001**, *12*, 510.
- (4) Kato, H.; Kanazawa, Y.; Okumura, M.; Taninaka, A.; Yokawa, T.; Shinohara, H. *J. Am. Chem. Soc.* **2003**, *125*, 4391.
- (5) Takata, M.; Nishibori, E.; Sakata, M.; Inakuma, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* **1999**, *83*, 2214.
- (6) Nishibori, E.; Takata, M.; Sakata, M.; Taninaka, A.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2998.
- (7) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maita, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55.
- (8) Kroto, H. W. *Nature* **1987**, *329*, 529.
- (9) Wang, C.-R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Nature* **2001**, *408*, 426. Takata, M.; Nishibori, E.; Wang, C. R.; Sakata, M.; Shinohara, H. *Chem. Phys. Lett.* **2003**, *372*, 512.
- (10) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamp, J. C.; Rice, G.; Glass, T.; Harich, K.; Hadju, E.; Bible, R.; Dorn, H. C. *Nature* **2001**, *408*, 428.
- (11) Wan, T. S. M.; Zhang, H.-W.; Nakane, T.; Xu, Z.; Inakuma, M.; Shinohara, H.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1998**, *120*, 6896.
- (12) Mass spectral measurements indicate the presence of  $C_{72}$ , but extraction and separation of  $C_{72}$  have not yet been done. The existence of a peak corresponding to  $C_{72}$  does not necessarily indicate the actual presence of the fullerene because  $C_{72}$  fragments from other higher fullerenes are oftentimes produced at the time of ionization.
- (13) Wang, C.-R.; Shinohara, H., to be published.
- (14) Stevenson, S.; Burbank, P.; Harich, K.; Sun, Z.; Dorn, H. C.; van Loosdrecht, P. H. M.; deVries, M. S.; Salem, J. R.; Kiang, C.-H.; Johnson, R. D.; Bethune, D. S. *J. Phys. Chem. A* **1998**, *102*, 2833.
- (15) Dunsch, L.; Bartl, A.; Georgi, P.; Kuran, P. *Synth. Met.* **2001**, *121*, 1113.
- (16)  $C_{74}$  can be extracted by basic organic solvents such as pyridine and DMF. The isolation of the  $C_{74}$  has not yet been achieved, because  $C_{74}$  is insoluble in HPLC solvents such as toluene and  $\text{CS}_2$ .
- (17) Fujii, R.; Kodama, T.; Miyake, Y.; Suzuki, S.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K.; Achiba, Y., to be published.
- (18) Okazaki, T.; Lian, Y.; Gu, Z.; Suenaga, K.; Shinohara, H. *Chem. Phys. Lett.* **2000**, *320*, 435.
- (19) Kuran, P.; Krause, M.; Bartl, A.; Dunsch, L. *Chem. Phys. Lett.* **1998**, *292*, 580.
- (20) Dorn, H. C.; Stevenson, S.; Burbank, P.; Harich, K.; Sun, Z.; Glass, T.; Anderson, M.; Bethune, D. S.; Sherwood, M. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 6, p 990.
- (21) Amman, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.
- (22) Akasaka, T.; Nagase, S.; Kobayashi, K.; Waelchli, W.; Yamamoto, K.; Funasaka, H.; Kako, M.; Hoshino, T.; Erata, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1643.
- (23) Kobayashi, K.; Nagase, S.; Yoshida, M.; Osawa, E. *J. Am. Chem. Soc.* **1997**, *119*, 12693.
- (24) Yamamoto, C.; Hayashi, T.; Okamoto, Y.; Ohkubo, S.; Kato, T. *Chem. Commun.* **2001**, 925.
- (25) Hawkins, J. M.; Meyer, A. *Science* **1993**, *260*, 1918.

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