Pentagonal-Dodecahedral La_2 Charge Density in [80-I_h]Fullerene: $La_2@C_{80}$**

Eiji Nishibori, Masaki Takata,* Makoto Sakata,
Atsushi Taninaka, and Hisanori Shinohara

New types of endohedral metallofullerenes[1] have been synthesized and structurally characterized in the past few years.[2] In particular, interesting behavior of metal atoms trapped inside carbon cages were revealed by structural studies, e.g. giant thermal motion;[3] formation of metal clusters,[2a] metal nitrides,[2b] and metal carbides;[2e] and violation of the isolated pentagon rule (IPR).[2c,d] These characteristic features were specific to metallofullerenes and closely related to the cage symmetry and the electrostatic interaction between the metal atoms and the carbon cage, which results from charge transfer from metal atoms to the carbon cage.

$La_2@C_{80}$ was one of the first endohedral metallofullerenes, and was produced in macroscopic amounts as early as 1991. It was also the first endohedral dimetallofullerene.[4] Although the cage symmetry of C_{80} was determined to be I_h, similar to that of C_{60}, from ab initio theoretical calculations[5] and ^{13}C NMR spectroscopy,[6] the endohedral structure of $La_2@C_{80}$ remained unknown. Here we report a novel feature of $La_2@C_{80}$, in which a perfect pentagonal-dodecahedral charge density of La_2 was detected in an icosahedral I_h-C_{80} cage by a synchrotron radiation (SR) structural study. The characteristic charge density results from a highly selective trajectory of the two La atoms, which hop along the hexagonal rings of the I_h-C_{80} polyhedral network.

The structural analysis was performed by means of SR powder diffraction. The experimental data were analyzed by the MEM/Rietveld method,[7] a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis. The structures of endohedral metallofullerenes such as $Y@C_{82}$,[7a] $Sc@C_{82}$,[8] $La@C_{82}$,[3] $Sc_2@C_{84}$,[9] $Sc_3@C_{82}$,[2a] $Sc_2@C_{66}$,[2e] and $Sc_2C_2@C_{84}$[2c] were successfully visualized as charge densities by using synchrotron radiation powder-diffraction data. Details of this method are described elsewhere.[7, 9]

The cell parameters (monoclinic, space group $P2_1$) were determined as $a = 18.2872(8)$, $b = 11.2120(4)$, $c = 11.1748(4)$ Å, and $\beta = 107.91(1)°$ by Rietveld analysis. The reliability (R) factor based on the Bragg intensities R_I and the weighted profile R factor R_{wp} were 6.3 and 2.6 %, respectively. Figure 1 shows the result of Rietveld fitting. The number of structure factors derived in this analysis was 502. The MEM charge density was derived from these structure factors by dividing the unit cell into 128 × 72 × 72 pixels. The R factor of the final MEM charge density was 3.8 %.

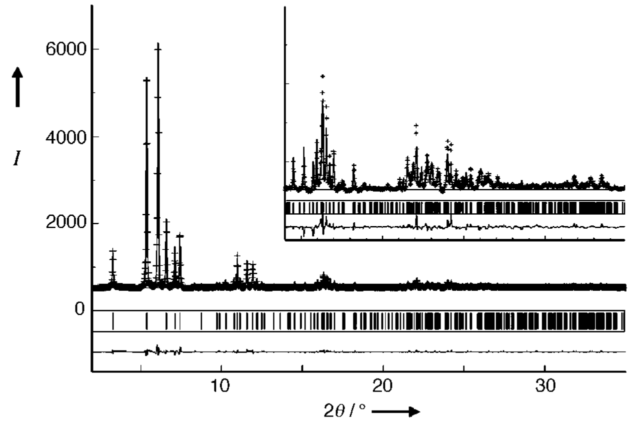

Figure 1. The result of Rietveld fitting for $La_2@C_{80}$. A closeup of the region between 14.0 and 35.0° is shown in the insert. The reliability factors are $R_I = 6.3$ % and $R_{wp} = 2.6$ %.

A three-dimensional representation of the $La_2@C_{80}$ molecule is shown in Figure 2 as a surface of equal charge density (1.7 e Å^{-3}). The MEM charge density clearly reveals six- and five-membered rings consistent with the reported I_h symmetry of the C_{80} cage. Figures 2 a and b represent the top views along S_{10} and C_2 axis of I_h-C_{80}, respectively. A pentagonal-dodecahedral cage (brown), which is presumably due to the charge density of the encaged La atoms, is clearly recognizable inside the C_{80} cage. The inner dodecahedral cage is also shown separately.

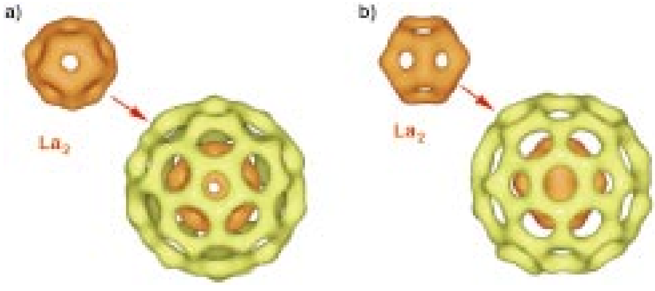

Figure 2. MEM charge densities of $La_2@C_{80}$ as the equal-density (1.7 e Å^{-3}) contour surface along the a) S_{10} and b) C_2 axes. The La_2 dodecahedral charge density is colored brown and is additionally shown beside the fullerene molecule.

To confirm that the charge density of this dodecahedral cage stems from the La atoms encapsulated in the C_{80} cage, we counted the total charge of this internal polyhedron. The total charge, calculated on the basis of the MEM results, is 108.8 e, which is very close to the number of electrons for two La^{3+} ions (108 e). We therefore conclude that the internal dodecahedron represents the distribution of two La^{3+} encapsulated in

---

[*] Prof. Dr. M. Takata, Dr. E. Nishibori, Prof. Dr. M. Sakata
Department of Applied Physics, Nagoya University
Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-4455
E-mail: a41024a@nucc.cc.nagoya-u.ac.jp
A. Taninaka, Prof. Dr. H. Shinohara
Department of Chemistry, Nagoya University
Nagoya 464-8602 (Japan)

[**] This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, JSPS Future Program on New Carbon Nano-Materials, and the TARA Sakabe Project. This work was also supported by the Toyota-Riken, the Murata Science Foundation, and the Sumitomo Foundation. The synchrotron radiation experiments were performed at SPring-8 BL02B2 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI).

the C_{80} cage; that is, the formal electronic structure is $(La^{3+})_2@C_{80}^{6-}$. The dodecahedral internal polyhedron therefore represents a time-averaged trajectory of the motion of two La atoms in the C_{80} cage. The entire $La_2@C_{80}$ molecule possesses the same I_h symmetry as I_h-C_{80}, since each pentagon of the dodecahedral charge density is faces a pentagonal ring of the C_{80} cage. This is consistent with previous ^{139}La and ^{13}C NMR studies, which suggested that the molecule has I_h symmetry.[6] The observed longest La–La distance and the shortest La–C distance are 3.84(2) and 2.39(3) Å, respectively. These values can be compared with reported theoretical values (La–La 3.665, La–C 2.56 Å)[5] for the D_{2h}-symmetric structure of $La_2@C_{80}$, in which La atoms are assumed to be symmetrically located on the C_2 axis.

The section of the charge density through the six-membered rings of the I_h-C_{80} cage is shown in Figure 3. The section through the internal dodecahedral cage is totally homogeneous in density. This indicates that the two La atoms, separated by 3.84 Å, hop rapidly around the I_h-C_{80} cage with a trajectory that connects the hexagonal rings but not the pentagons of C_{80} within the timescale of NMR measurements (ca. 10^{-6} s) at room temperature. Such a highly selective trajectory for the internal motion of the encaged metal atoms has never been observed in any other endohedral metallofullerenes.

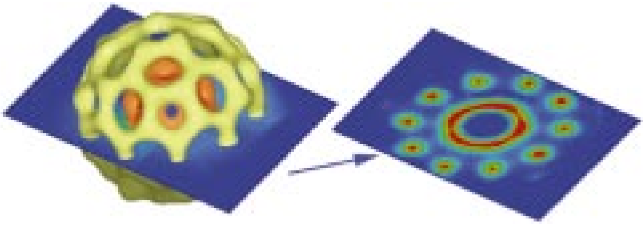

Figure 3. Section of charge density through the hexagonal rings of C_{80}. The homogeneous ring of charge density indicates an La_2 trajectory that connects the hexagonal rings of I_h-C_{80}.

In the La_2 dodecahedral feature, the presence of covalent bonding between the two La atoms might be expected. However, in the central region of the cage, there is no significant localized charge density (see Figure 3). This suggests ionic rather than covalent bonding character; that is, La_2 is not encaged as a dimer in the C_{80} cage.

Of the five Platonic solids, the cube, the tetrahedron, and the octahedron appear in crystals in nature, and the dodecahedron and the icosahedron have been seen in fullerenes, proteins, and viruses. However, no molecules or crystals in the form of a double-shell Platonic solid have been discovered in nature. Because of the I_h-C_{80} cage, a highly symmetrical charge density in the shape of a pentagonal dodecahedron results for the encaged La atoms, and this is the first example of a double-shell Platonic solid. This double-shell polyhedral structure is a novel form of endohedral metallofullerene and may be realized in other highly symmetrical fullerene cages such as C_{60}.

Experimental Section

A soot sample containing $La_2@C_{80}$ and other La metallofullerenes was produced in dc (300–400 A) spark mode under He flow at 50–80 Torr. $La_2@C_{80}$ was isolated by two-stage HPLC. The details of production and separation of $La_2@C_{80}$ is the same as for $Y@C_{82}$ and $Sc@C_{82}$ and described in detail elsewhere.[1,2c] The purity of $La_2@C_{80}$ relative to other fullerenes was greater than 99.9%, as determined by LD-TOF mass spectrometry and HPLC. The $La_2@C_{80}$ powder specimen was grown from toluene solution. The powder sample was sealed in a silica glass capillary (0.3 mm internal diameter).

The synchrotron radiation X-ray powder experiment with imaging plate (IP) detectors was carried out on the large Debye–Scherrer camera at SPring-8 BL02B2. The exposure time was 6 h. The wavelength of incident X-rays was 1.0 Å. The X-ray powder pattern of $La_2@C_{80}$ was obtained in 0.02° steps in 2θ from 3.0 to 35.0°, which corresponds to 1.66 Å resolution in *d*-spacing.

Received: April 18, 2001 [Z16958]

---

[1] H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843–892.

[2] a) M. Takata, E. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1999**, *83*, 2214–2217; b) S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature* **1999**, *401*, 55–57; c) C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2000**, *408*, 426–427; d) S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2000**, *408*, 427–428; e) C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Angew. Chem.* **2001**, *113*, 411–413; *Angew. Chem. Int. Ed.* **2001**, *40*, 397–399.

[3] E. Nishibori, M. Takata, M. Sakata, H. Tanaka, M. Hasegawa, H. Shinohara, *Chem. Phys. Lett.* **2000**, *330*, 497–502.

[4] M. M. Alvarez, E. G. Gillan, K. Holczer, R. B. Kaner, K. S. Min, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 10561–10563.

[5] K. Kobayashi, S. Nagase, K. Akasaka, *Chem. Phys. Lett.* **1995**, *245*, 230–236.

[6] T. Akasaka, S. Nagase, K. Kobayashi, M. Wälchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata, *Angew. Chem.* **1997**, *109*, 1716–1719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1643–1645.

[7] a) M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, H. Shinohara, *Nature* **1995**, *377*, 46–49; b) M. Takata, E. Nishibori, M. Sakata, *Z. Kristallogr.* **2001**, *216*, 71–86.

[8] E. Nishibori, M. Takata, M. Sakata, M. Inakuma, H. Shinohara, *Chem. Phys. Lett.* **1998**, *298*, 79–84.

[9] M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1997**, *78*, 3330–3333.

0044-8249/01/11316-3087 $ 17.50+.50/0