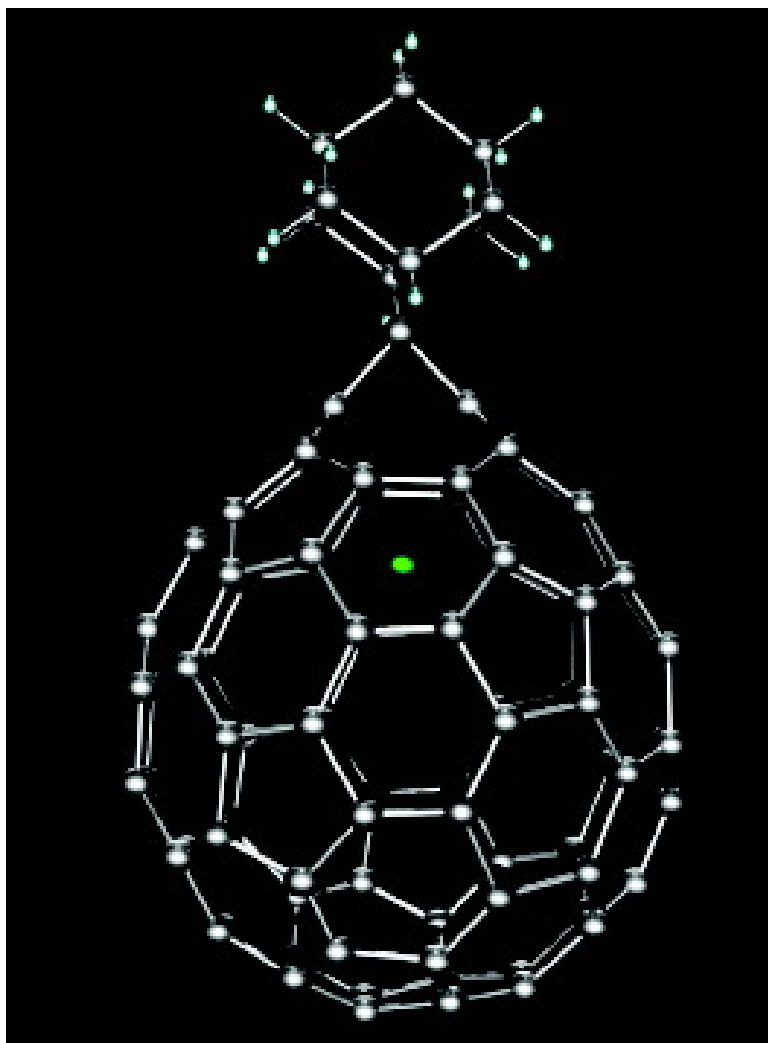


Does Gd@C Have an Anomalous Endohedral Structure? Synthesis and Single Crystal X-ray Structure of the Carbene Adduct

Takeshi Akasaka, Takayoshi Kono, Yuji Takematsu, Hidefumi Nikawa, Tsukasa Nakahodo, Takatsugu Wakahara, Midori O. Ishitsuka, Takahiro Tsuchiya, Yutaka Maeda, Michael T. H. Liu, Kenji Yoza, Tatsuhiisa Kato, Kazunori Yamamoto, Naomi Mizorogi, Zdenek Slanina, and Shigeru Nagase

J. Am. Chem. Soc., 2008, 130 (39), 12840-12841 • DOI: 10.1021/ja802156n • Publication Date (Web): 09 September 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Does Gd@C₈₂ Have an Anomalous Endohedral Structure? Synthesis and Single Crystal X-ray Structure of the Carbene Adduct

Takeshi Akasaka,^{*,†} Takayoshi Kono,[†] Yuji Takematsu,[†] Hidefumi Nikawa,[†] Tsukasa Nakahodo,[†] Takatsugu Wakahara,[†] Midori O. Ishitsuka,[†] Takahiro Tsuchiya,[†] Yutaka Maeda,[‡] Michael T. H. Liu,[§] Kenji Yoza,^{||} Tatsuhisa Kato,[⊥] Kazunori Yamamoto,[#] Naomi Mizorogi,[○] Zdenek Slanina,[†] and Shigeru Nagase^{*,○}

Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba 305-8577, Japan, Department of Chemistry, Tokyo Gakugei University, Koganei 184-8501, Japan, Department of Chemistry, University of Prince Edward Island, Prince Edward Island C1A4P3, Canada, Bruker AXS K. K., Yokohama 221-0022, Japan, Department of Chemistry, Josai University, Sakado 171-8501, Japan, Japan Atomic Energy Agency, Tokai 319-1100, Japan, and Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

Received March 26, 2008; Revised Manuscript Received August 23, 2008; E-mail: akasaka@tara.tsukuba.ac.jp

Endohedral metallofullerenes have attracted considerable interest as promising spherical molecules for material and biomedical applications, because of their unique properties that are unexpected from empty fullerenes.¹ It is the focus of interest to determine cage structures and metal positions, because these are essential for the properties and reactivities of endohedral metallofullerenes. Since the first extraction of La@C₈₂ in 1991,² M@C₈₂ (M = group 3 metals and lanthanides) has been known as a representative monometallofullerene. Theoretical calculations have predicted that the M atom is mostly encapsulated inside the C_{2v} cage of C₈₂.^{3,4} This prediction has been verified for metals such as M = Y,⁵ La,^{6–8} Ce,⁹ and Pr¹⁰ by measuring the ¹³C NMR spectra of the diamagnetic anion of M@C₈₂ or from the X-ray crystal analysis of the La@C₈₂ carbene adduct.⁷ The C_{2v} cage structures of Sc@C₈₂¹¹ and La@C₈₂¹² have been also found by the MEM (maximum entropy method)/Rietveld analysis of synchrotron X-ray powder diffraction data. In addition, the MEM/Rietveld analysis has shown that the Sc and La atoms are located at an off-centered position near a hexagonal ring of the C_{2v}-C₈₂ cage. This agrees with theoretical prediction.⁴ The X-ray single crystal analysis and theoretical calculations of La@C₈₂(Ad) (Ad = adamantylidene) have revealed that the La position is little changed by the Ad addition.⁷ The paramagnetic NMR spectral analysis and theoretical calculations of Ce@C₈₂ and its anion have shown that the Ce atom even in the Ce@C₈₂ anion is also located at an off-centered position adjacent to a hexagonal ring along the C₂ axis of the C_{2v}-C₈₂ cage.¹³

From the MEM/Rietveld analysis, however, it has been recently claimed that Gd@C₈₂¹⁴ and Eu@C₈₂¹⁵ have an exceptional anomalous endohedral structure, in which the metal atom having f electrons is located near the C–C double bond on the opposite side of the C_{2v}-C₈₂ cage along the C₂ axis. This claim disagrees with theoretical calculations^{4,16–18} and experimental studies.^{19,20} According to the recent theoretical calculations of Gd@C₈₂ and Eu@C₈₂, the anomalous structures found from the MEM/Rietveld analysis are highly unstable and do not correspond to energy minima.¹⁷ In this context, we have carried out the single crystal X-ray crystallographic analysis of the Gd@C₈₂ carbene adduct

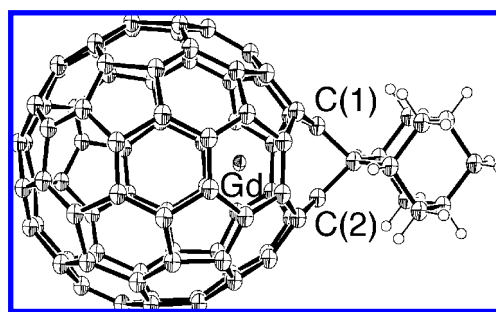
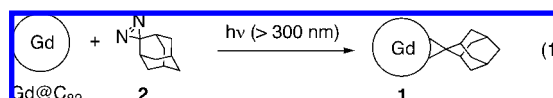


Figure 1. ORTEP drawing of one enantiomeric isomer of Gd@C₈₂(Ad) (1) showing thermal ellipsoids at the 50% probability level. The CS₂ and 1,2,4-trichlorobenzene molecules are omitted for clarity.

(Gd@C₈₂(Ad)(1)) together with theoretical calculations. These results do not support the anomalous structure of Gd@C₈₂.

Irradiation of a toluene solution of Gd@C₈₂²¹ (2 mg, 7.8 × 10^{−5} M) and an excess molar amount of 2-adamantane-2,3-[3H]-diazirine (2) in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 300 nm) resulted in the formation of the adduct, Gd@C₈₂(Ad) (1) in a 95% yield, which was purified by preparative HPLC (eq 1). LD-TOF mass spectrometry of 1 (C₉₂H₁₄Gd, mass *m/z* 1410) exhibits a molecular ion peak at *m/z* 1410–1407 and a peak at *m/z* 1276–1273 (Gd@C₈₂) due to the loss of the Ad group. The UV–visible-near-infrared absorption spectrum of 1 is similar to that of the pristine Gd@C₈₂. These results suggest that 1 retains the essential electronic and structural character of Gd@C₈₂.



The structure of 1 determined by the X-ray crystal analysis²² is shown in Figure 1. The structural aspects are very similar to those for La@C₈₂(Ad). As is apparent from Figure 1, the fullerene cage of 1 originates from the C_{2v} isomer of C₈₂ and the Gd atom is located at a single site. It is notable that the Gd atom is located at an off-centered position near a hexagonal ring in the C_{2v}-C₈₂ cage, as found for M@C₈₂ (M = Sc¹¹ and La¹²) and La@C₈₂(Ad).⁷ The C(1)–C(2) distance is 2.100 Å, indicative of an open structure. The Gd–C(1) and Gd–C(2) distances are 2.515 and 2.523 Å, respectively. The X-ray data collected at 90, 213, and 293 K reveal

[†] University of Tsukuba.

[‡] Tokyo Gakugei University.

[§] University of Prince Edward Island.

^{||} Bruker AXS K. K.

[⊥] Josai University.

[#] Japan Atomic Energy Agency.

[○] Institute for Molecular Science.

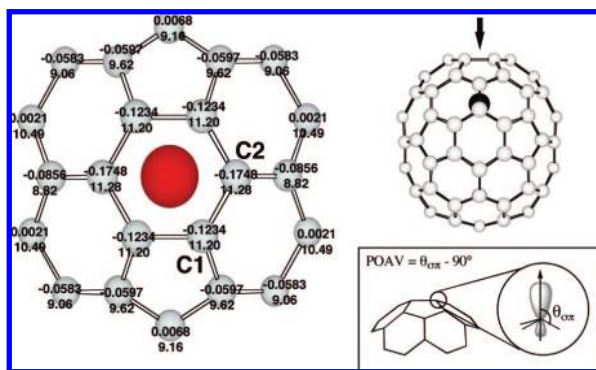


Figure 2. Selected charge densities (upper) and POAV ($\theta_{OA} - 90^\circ$) values (lower) in Gd@C₈₂.

that the Gd atom remains at the same position regardless of temperatures, as shown in Figure 1.

Since there are 24 nonequivalent carbons and 19 nonequivalent 6–6 bonds in Gd@C₈₂, the addition of Ad may occur at several sites to afford several monoadduct isomers. Although the reactions of Gd@C₈₂ with organic reagents²³ have been reported so far, no structural determination of the adducts has been reported yet.

The selective formation of **1** (the structure in Figure 1) can be explained using the reaction of the photochemically generated Ad with Gd@C₈₂, as in the La@C₈₂ case.⁷ The local strain on cage carbons plays an important role in determining the reactivity. The pyramidalization angles from the π -orbital axis vector analysis POAV ($\theta_{OA} - 90^\circ$) values provide a useful index of the local strain.²⁴ The Mulliken charge densities and POAV ($\theta_{OA} - 90^\circ$) values calculated for Gd@C₈₂ are shown in Figure 2.²⁵ Both values are found to be large for the carbons in the six-membered ring nearest to the Gd atom. This suggests that the electrophilic Ad selectively attacks the highly electron-rich and strained carbons in the six-membered ring.²⁶ In fact, the addition of Ad takes place on the carbon atoms, C(1) and C(2) (Figure 2), as indicated by the X-ray crystal structure (Figure 1). The structural confirmation of Gd@C₈₂ by X-ray single crystal structure analysis is in progress and will be reported in due course.

The single crystal X-ray crystallographic analysis of Gd@C₈₂(Ad) (**1**) suggests that Gd@C₈₂ has a normal endohedral structure in which the Gd atom is located at an off-centered position near a hexagonal ring (not near the C–C double bond) along the C₂ axis of the C_{2v}-C₈₂ cage, as does M@C₈₂ (M = Sc¹¹ and La¹²). This indicates that the MEM/Rietveld analysis is not always reliable for metal positions^{17,27} as well as cage structures,^{28,29} though it has been widely used for structural determination of endohedral metallofullerenes.³⁰ The highly selective derivatization of Gd@C₈₂ suggests that an encapsulated metal plays an important role in controlling the reactivity and selectivity of fullerenes. Synthesis of target molecules with a high selectivity and reactivity is important for accurate organic synthesis, especially for endohedral metallofullerenes whose preparation and isolation are difficult in large-scale quantities.

Acknowledgment. This work was supported in part by a Grant-in-Aid, the 21st Century COE Program, Nanotechnology Support

Project, The Next Generation Super Computing Project (Nanoscience Project), and Scientific Research on Priority Area from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: Complete refs 6 and 7; analytical HPLC profile and cyclic and differential pulse voltammogram of **1**; details of theoretical calculation and the X-ray crystallographic data collection and structure refinement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Akasaka, T.; Nagase, S., Eds. *Endofullerenes: A New Family of Carbon Clusters*; Kluwer: Dordrecht, The Netherlands, 2002.
- (2) Chai, Y.; Guo, T.; Jin, C.; Haulfler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; M.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564–7568.
- (3) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Oxford Univ. Press: Oxford, U.K., 1995.
- (4) Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **1998**, *282*, 325–329.
- (5) Feng, L.; Wakahara, T.; Tsuchiya, T.; Maeda, Y.; Lian, Y.; Akasaka, T.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **2005**, *405*, 274–277.
- (6) Akasaka, T.; et al. *J. Am. Chem. Soc.* **2000**, *122*, 9316–9317.
- (7) Maeda, Y.; et al. *J. Am. Chem. Soc.* **2004**, *126*, 6858–6859.
- (8) Tsuchiya, T.; Wakahara, T.; Maeda, Y.; Akasaka, T.; Waelchli, M.; Kato, T.; Okubo, H.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 3282–3285.
- (9) Wakahara, T.; Kobayashi, J. -I.; Yamada, M.; Maeda, Y.; Tsuchiya, T.; Okamura, M.; Akasaka, T.; Waelchli, M.; Kobayashi, K.; Nagase, S.; Kato, T.; Kako, M.; Yamamoto, K.; Kadish, K. M. *J. Am. Chem. Soc.* **2004**, *126*, 4883–4887.
- (10) Wakahara, T.; Okubo, S.; Kondo, M.; Maeda, Y.; Akasaka, T.; Waelchli, M.; Kako, M.; Kobayashi, K.; Nagase, S.; Kato, T.; Yamamoto, K.; Gao, X.; Caemelbecke, G. E.; Kadish, K. M. *Chem. Phys. Lett.* **2002**, *360*, 235–239.
- (11) Nishibori, E.; Takata, T.; Sakata, M.; Inakuma, M.; Shinohara, H. *Chem. Phys. Lett.* **1998**, *298*, 79–84.
- (12) Nishibori, E.; Takata, M.; Sakata, M.; Tanaka, H.; Hasegawa, M.; Shinohara, H. *Chem. Phys. Lett.* **2000**, *330*, 497–502.
- (13) Yamada, M.; Wakahara, T.; Lian, Y.; Tsuchiya, T.; Akasaka, T.; Waelchli, M.; Mizorogi, N.; Nagase, S.; Kadish, K. M. *J. Am. Chem. Soc.* **2006**, *128*, 1400–1401.
- (14) Nishibori, E.; Iwata, K.; Sakata, M.; Takata, M.; Tanaka, H.; Kato, H.; Shinohara, H. *Phys. Rev. B* **2004**, *69*, 113412.
- (15) Sun, B. -Y.; Sugai, T.; Nishibori, E.; Iwata, K.; Sakata, M.; Takata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4568–4571.
- (16) Senapati, L.; Schrier, J.; Whaley, K. B. *Nano Lett.* **2004**, *4*, 2073–2078.
- (17) Mizorogi, N.; Nagase, S. *Chem. Phys. Lett.* **2006**, *431*, 110–112.
- (18) Senapati, L.; Schrier, J.; Whaley, K. B. *Nano Lett.* **2005**, *5*, 2341.
- (19) Giefers, H.; Nessel, F.; Gyory, S. I.; Strecker, M.; Wortmann, G.; Grushko, Y. S.; Alekseev, E. G.; Koslov, V. S. *Carbon* **1999**, *37*, 721–725.
- (20) Liu, L.; Gao, B.; Chu, W.; Chen, D.; Hu, T.; Wang, C.; Dunsch, L.; Marcelli, A.; Luo, Y.; Wu, Z. *Chem. Commun.* **2008**, 474–476.
- (21) Lian, Y.; Shi, Z.; Zhou, X.; He, X.; Gu, Z. *Chem. Mater.* **2001**, *13*, 39–42.
- (22) See the Supporting Information for crystal data of Gd@C₈₂(Ad)(**1**).
- (23) Lu, X.; He, X.; Feng, L.; Shi, Z.; Gu, Z. *Tetrahedron* **2004**, *60*, 3713–3716.
- (24) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.
- (25) See the Supporting Information.
- (26) (a) Moss, R. A.; Chang, M. *J. Tetrahedron Lett.* **1981**, *22*, 3749–3752. (b) Bonneau, R.; Hellrung, B.; Liu, M. T. H.; Wirz, J. *J. Photochem. Photobiol., A* **1998**, *116*, 9–19.
- (27) The recent density functional calculation of La@C₈₂(Jin, P.; Hao, C.; Li, S.; Mi, W.; Sun, Z.; Zhang, J.; Hou, Q. *J. Phys. Chem. A* **2007**, *111*, 167–169) suggests that the La atom can oscillate only around the energy minimum. This is apparently inconsistent with the giant bowl-shaped movement found by the MEM/Rietveld analysis.¹²
- (28) Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; Liu, M. T. H.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 12500–12501.
- (29) Iiduka, Y.; Wakahara, T.; Nakajima, K.; Nakahodo, T.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Liu, M. T. H.; Mizorogi, N.; Nagase, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5562–5564.
- (30) For a recent review, see: Takata, M. *Acta Crystallogr.* **2008**, *A64*, 232–245.

JA802156N