Endohedral Fullerenes

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Isolation and Structural Characterization of the Molecular Nanocapsule $Sm_2@D_{3d}(822)\text{-}C_{104}$**

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We report the isolation and structural characterization of the nanocapsule $Sm_2@D_{3d}(822)\text{-}C_{104}$. This remarkable molecule is the largest endohedral fullerene to be crystallographically characterized to date and is nearly twice the size of the prototypical C_{60}. The carbon cages in endohedral fullerenes involving metal atom encapsulation are generally larger than C_{60}. Considerable effort has been expended in characterizing endohedral fullerenes with 80, 82, or 84 carbon atoms.[1] Endohedral fullerenes containing M_3N units can be obtained in yields that are better than those of endohedrals with only metal atoms inside.[2,3] For endohedrals of the type $M_3N@C_{2n}$, metal atom size affects the size of the fullerene cage that forms.[4–6] With a small metal atom like scandium, the family of endohedrals $Sc_3N@C_{80}$ (I_h and D_{5h} isomers), $Sc_3N@D_{3h}\text{-}C_{78}$, and $Sc_3N@D_3\text{-}C_{68}$ form.[2] But with a bigger metal atom, cerium, Echegoyen and co-workers observed the formation of cages as large as $Ce_3N@C_{104}$.[7,8] Large fullerene cages can also form around only one or two metal atoms. A series of endohedrals containing two gadolinium atoms extending from Gd_2C_{90} to Gd_2C_{124} has been detected and pure samples of two isomers of Gd_2C_{94} and the complete series from Gd_2C_{96} to Gd_2C_{106} have been obtained.[9] Of these, $Gd_2C_2@D_3(85)\text{-}C_{92}$ has been structurally characterized by X-ray diffraction.[9] Prior to the present work, the largest endohedral fullerenes to be fully structurally characterized were the monometallic endohedrals, $Tm@C_{3v}\text{-}C_{94}$ and $Ca@C_{3v}\text{-}C_{94}$.[10] Poblet and co-workers have examined the possible structures of carbon cages in the size range C_{92} to C_{100}, in which there is a formal transfer of six electrons from a M_3N cluster or a M_2 unit to the carbon cage. They noted the remarkable properties and stability of the $D_5(450)\text{-}C_{100}$ cage, which is related to the I_h and D_{5h} isomers of C_{80} through dividing the cage in half perpendicular to the five-fold axis and adding an array of 20 carbon atoms between the two halves.[11]

Carbon soot containing samarium-based endohedral fullerenes was obtained by vaporizing a graphite rod filled with Sm_2O_3 and graphite powder in an electric arc as outlined earlier.[12] The carbon soot was extracted with *o*-dichlorobenzene and the soluble extract was subjected to a four-stage high pressure liquid chromatographic (HPLC) isolation process. Three individual isomers of $Sm_2@C_{104}$ were separated and purified. These isomers are labeled $Sm_2@C_{104}$(I), $Sm_2@C_{104}$(II), and $Sm_2@C_{104}$(III) in order of their elution times (29.4 (I), 30.0 (II) and 31.5 min (III), Buckyprep column, chlorobenzene eluent) during chromatography. The relative abundances of the isolated isomers are 1 (I):0.6 (II):0.2 (III). UV/Vis/NIR absorption spectra of the individual isomers are shown in Figure 1. Figure 2 shows the laser-desorption time-of-flight (LD-TOF) mass spectrum of the purified sample of the first isomer to elute, $Sm_2@C_{104}$(I), which was utilized in the crystallographic studies.

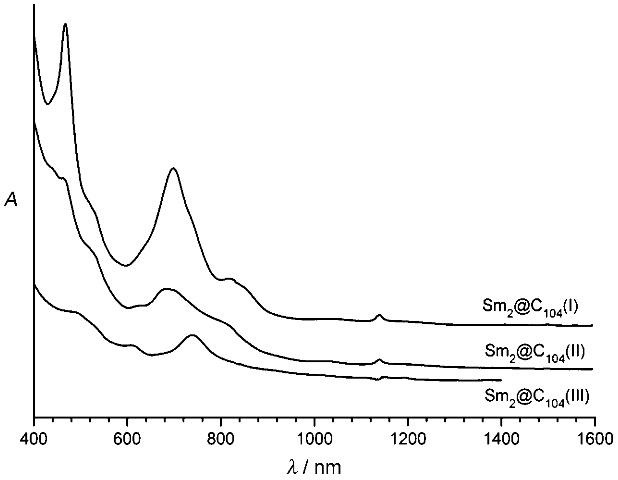

Figure 1. UV/Vis/NIR absorption spectra of $Sm_2@C_{104}$(I, II, III) in chlorobenzene solution.

Black parallelepipeds of $Sm_2@D_{3d}(822)\text{-}C_{104}\cdot 2\,Ni(oep)\cdot C_6H_5Cl$ were obtained by allowing chlorobenzene solutions of $Sm_2@C_{104}$(I) and of nickel octaethylporphyrin, [Ni(oep)], to diffuse together. Fortunately, the crystal utilized in the structural study was not marred by disorder of the fullerene cage that plagues structural characterization of many other endohedral fullerenes. The asymmetric unit

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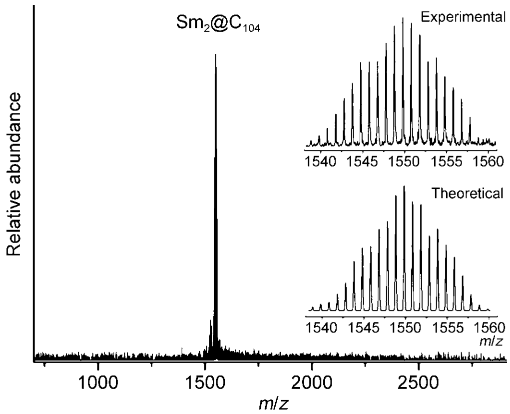

Figure 2. LD-TOF mass spectrum (positively charged spectrum) of a purified sample of $Sm_2@C_{104}$(I). The insets show expansions of the experimental and theoretical spectra for the parent ion.

consists of one molecule of [Ni(oep)], one-half of the endohedral with the other half generated by a center of symmetry, and one-half of a disordered chlorobenzene molecule. Figure 3 shows a drawing of the endohedral and the two surrounding molecules of [Ni(oep)]. Endohedral fullerenes like $Sm_2@C_{104}$(I) with the composition M_2C_{2n} may exist as a conventional endohedral, $M_2@C_{2n}$, (e.g. $Er_2@C_s(6)$-C_{82},[13] $Er_2@C_{3v}(8)$-C_{82}[14]), or as a carbide, $M_2C_2@C_{2n-2}$ (e.g. $Sc_2C_2@D_{2d}$-C_{84},[15] $Gd_2C_2@D_3(85)$-C_{92}[9]). The crystallographic data indicate that $Sm_2@C_{104}$(I) is a conventional endohedral and not a carbide. $Sm_2@C_{104}$(I) utilizes a carbon cage with D_{3d} symmetry, specifically the $D_{3d}(822)$-C_{104} cage, which is one of 823 isomers of C_{104} that obey the isolated pentagon rule and the only one with D_{3d} symmetry.[16]

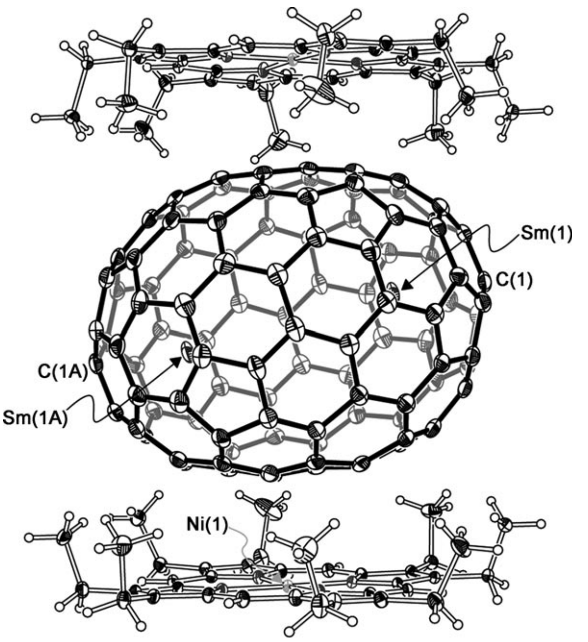

Figure 3. Two molecules of [Ni(oep)] surround the molecule of $Sm_2@D_{3d}(822)$-C_{104}. For clarity, the chlorobenzene molecules were omitted from this drawing and only the major sites (with 0.74 fractional occupancy) for the samarium atoms are shown.

There is some disorder in the positions of the samarium atoms. The major site, which is the only one shown in Figure 3, has 0.74 fractional occupancy, but there are two nearby sites with 0.17 and 0.09 occupancy. In the complete molecule, the two primary samarium atoms are located near the threefold axis of the cage and are separated by 5.8322(7) Å. Each samarium atom lies beneath a canopy of three adjacent hexagonal rings as shown in Figure 4. The Sm−C1 distance (2.521(5) Å) is the shortest Sm−C distance in the molecule.

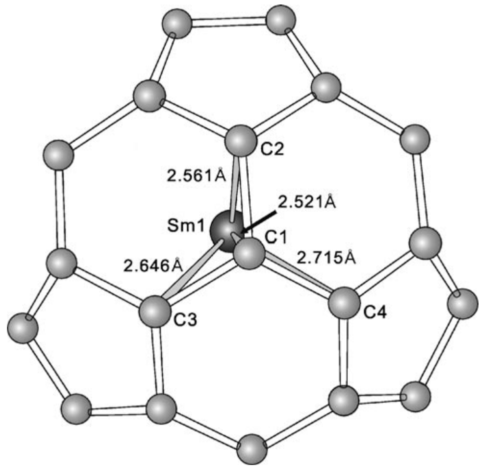

Figure 4. Structure of $Sm_2@D_{3d}(822)$-C_{104} showing the interactions between the major site for the samarium ion and the closest carbon atoms within the cage. The standard deviation for the Sm−C distances is 0.005 Å.

This cage has a clearly elongated structure that is closely related to that of a capped armchair carbon nanotube and to the structure of the I_h and D_{5h} isomers of C_{80}.[17] The length of the cage, as measured by the distance between the two carbon atoms (C1 and C1A) that lie on the threefold axis, is 10.840(9) Å, while its diameter is 8.264(9) Å. The I_h-C_{80} cage can be bisected in three different ways: by cutting perpendicular to the C_5, C_3, and C_2 axes of the molecule, respectively. As noted earlier, cutting perpendicular to the C_5 axis and adding 20 carbon atoms produces $D_5(450)$-C_{100}. When the I_h-C_{80} cage is cut perpendicular to the C_3 axis, addition of 24 carbon atoms produces the $D_{3d}(822)$-C_{104} cage. Figure 5 shows that the structure of the cage in $Sm_2@D_{3d}$-(822)-C_{104} is comprised of two caps whose structures are based on I_h-C_{80}, with the addition of 24 carbon atoms, which are shown as solid gray circles. A number of computational studies have explored the interactions between the end-caps and walls of various capped carbon nanotubes, and the effects of these interactions on the structure and physical properties of these tubes.[17–19] Generally, these studies have focused on a hemisphere of C_{60} as the capping group. However, the I_h-C_{80} cage also provides a capping group that appears to be significant in the structures of endohedral fullerene nanocapsules and may be found in capped carbon nanotubes.

Computational data suggest the $Sm_2@D_{3d}(822)$-C_{104} has the electronic distribution $(Sm^{2+})_2@[D_{3d}(822)$-$C_{104}^{4-}]$. Figure 6 shows the molecular orbital energies computed for

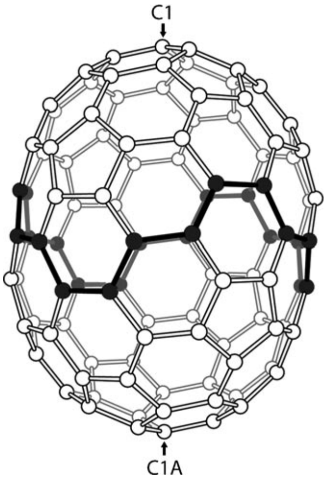

Figure 5. Structure of the D_{3d}(822)-C_{104} cage with the carbon atoms in two halves of an I_h-C_{80} cage shown as open circles and the added 24 carbon atoms shown as filled grey circles. The threefold axis is aligned vertically and runs through C1 and C1A.

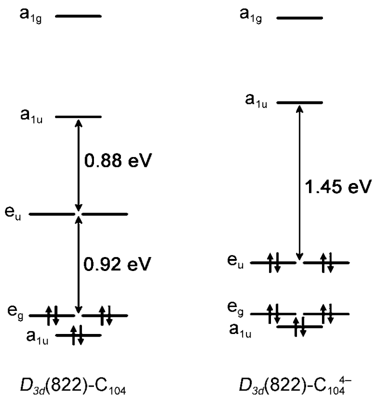

Figure 6. The energy levels of neutral and tetra-anion of D_{3d}(822)-C_{104} calculated at B3LYP density functions level with 3-21g(d) basis set.

the neutral and tetra-anionic forms of the empty cage D_{3d}(822)-C_{104} using DFT methodology at the B3LYP level. The additional four electrons in the tetra-anion are accommodated by the LUMO e_u level, and the e_u to a_{1u} gap in the tetra-anion increases to 1.45 eV in the tetra-anion.

In summary, the structural characterization of $Sm_2@D_{3d}$-(822)-C_{104} reveals that it is a member of a new class of nanocapsules with a carbon cage that resembles a small carbon nanotube with end caps based on the I_h-C_{80} structure.

Experimental Section

Crystal data for $Sm_2@D_{3d}$(822)-C_{104}·2 Ni(oep)·C_6H_5Cl: $C_{182}H_{93}ClN_8Ni_2Sm_2$, F.W. 2845.21, black parallelepiped, $0.012 \times 0.019 \times 0.015$ mm, monoclinic, space group $P2_1/n$, $a = 15.2821(10)$, $b = 17.6286(11)$, $c = 20.9966(12)$ Å, $\beta = 92.431(3)°$, $V = 5651.4(6)$ Å^3, $\lambda = 0.77490$ Å, Advanced Light Source beamline 11.3.1, $Z = 2$, $\rho_{\text{cald}} = 1.672$ Mg m^{-3}; $\mu = 1.814$ mm^{-1}; $T = 100(2)$ K; Bruker Apex II; $2\Theta_{\max} = 70°$; 70229 reflections collected, $R(\text{int}) = 0.032$; min/max transmission = 0.62/0.75 (multi-scan absorption correction applied); Patterson and difference Fourier methods solution (SHELXS97),[20] full-matrix least squares based on F^2 (SHELXL97);[20] $R = 0.0890$, $wR = 0.2069$ for 18520 unique data; conventional $R1 = 0.0710$ computed for 15455 observed data ($> 2\sigma(I)$) with no restraints and 889 parameters.

CCDC 744858 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Springer, Berlin, **2002**.
[2] 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.
[3] L. Dunsch, S. Yang, *Small* **2007**, *3*, 1298.
[4] S. Yang, L. Dunsch, *J. Phys. Chem. B* **2005**, *109*, 12320.
[5] S. Yang, L. Dunsch, *Chem. Eur. J.* **2006**, *12*, 413.
[6] T. Zuo, C. M. Beavers, J. C. Duchamp, A. Campbell, H. C. Dorn, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2007**, *129*, 2035.
[7] M. N. Chaur, F. Melin, B. Elliott, A. Kumbhar, A. J. Athans, L. Echegoyen, *Chem. Eur. J.* **2008**, *14*, 4594.
[8] F. Melin, M. N. Chaur, S. Engmann, B. Elliott, A. Kumbhar, A. J. Athans, L. Echegoyen, *Angew. Chem.* **2007**, *119*, 9190; *Angew. Chem. Int. Ed.* **2007**, *46*, 9032.
[9] H. Yang, C. Lu, Z. Liu, H. Jin, Y. Che, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2008**, *130*, 17296.
[10] Y. Che, H. Yang, Z. Wang, H. Jin, Z. Liu, C. Lu, T. Zuo, H. Dorn, C. M. Beavers, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **2009**, *48*, 6004.
[11] R. Valencia, A. Rodriguez-Fortea, J. M. Poblet, *Chem. Commun.* **2007**, 4161.
[12] D.-Y. Sun, Z.-Y. Liu, X.-H. Guo, W.-G. Xu, S.-Y. Liu, *J. Phys. Chem. B* **1997**, *101*, 3927.
[13] M. M. Olmstead, A. de Bettencourt-Dias, S. Stevenson, H. C. Dorn, A. L. Balch, *J. Am. Chem. Soc.* **2002**, *124*, 4172.
[14] M. M. Olmstead, H. M. Lee, S. Stevenson, H. C. Dorn, A. L. Balch, *Chem. Commun.* **2002**, 2688.
[15] C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Angew. Chem.* **2001**, *113*, 411; *Angew. Chem. Int. Ed.* **2001**, *40*, 397.
[16] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**.
[17] T. Yumura, S. Bandow, K. Yoshizawa, S. Iijima, *J. Phys. Chem. B* **2004**, *108*, 11426.
[18] T. Yumura, D. Nozaki, S. Bandow, K. Yoshizawa, S. Iijima, *J. Am. Chem. Soc.* **2005**, *127*, 11769.
[19] P. Politzer, P. Lane, M. C. Concha, J. S. Murray, *Microelectron. Eng.* **2005**, *81*, 485.
[20] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.