

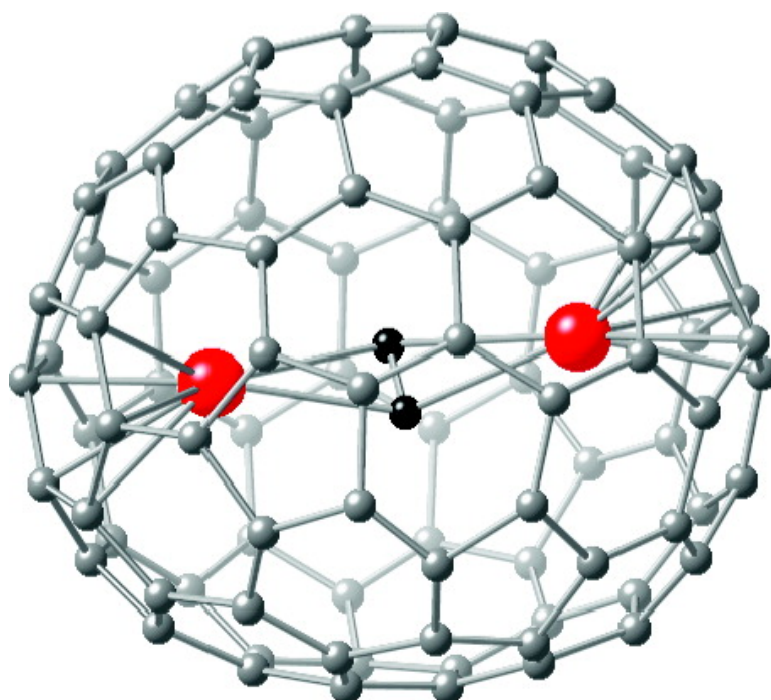
Article

Detection of a Family of Gadolinium-Containing Endohedral Fullerenes and the Isolation and Crystallographic Characterization of One Member as a Metal#Carbide Encapsulated inside a Large Fullerene Cage

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Detection of a Family of Gadolinium-Containing Endohedral Fullerenes and the Isolation and Crystallographic Characterization of One Member as a Metal–Carbide Encapsulated inside a Large Fullerene Cage

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Abstract: A series of di-gadolinium endohedrals that extends from Gd_2C_{90} to Gd_2C_{124} has been detected by mass spectrometry of the *o*-dichlorobenzene extract of the carbon soot produced by direct current arcing of graphite rods filled with a mixture of Gd_2O_3 and graphite powder. Chromatographic separation has led to the isolation of pure samples of two isomers of Gd_2C_{94} and the complete series from Gd_2C_{96} to Gd_2C_{106} . Endohedral fullerenes of the type M_2C_{2n} can exist as the conventional endohedral, $M_2@C_{2n}$, or as the carbide-containing endohedral, $M_2C_2@C_{2n-2}$. Crystallographic characterization of the more rapidly eluting isomer of Gd_2C_{94} reveals that it possesses the carbide structure, $Gd_2C_2@D_3(85)-C_{92}$. Computational studies suggest that the more slowly eluting isomer of Gd_2C_{94} may be a conventional endohedral, $Gd_2@C_2(121)-C_{94}$.

Introduction

Fullerenes with metal atoms trapped inside are undergoing vigorous study because of their potential applications in medicine and materials development.¹ Such endohedral fullerenes are known to encapsulate up to three individual metal atoms as well as clusters of the types M_3N ,² M_2C_2 ,^{3,4} M_3C_2 ,⁵ and M_4O_2 .⁶

The observation that the M_2C_2 unit can be trapped within a fullerene cage has interesting consequences regarding the structure of endohedrals with the composition M_2C_{2n} . Members of this group may exist as the conventional endohedral, $M_2@C_{2n}$, or as the carbide, $M_2C_2@C_{2n-2}$, and care needs to be taken to distinguish between these possibilities. A number of particularly well-characterized examples of the M_2C_{2n} class [*e.g.*, $Er_2@C_s(6)-$

C_{82} ,⁷ $Er_2@C_{3v}(8)-C_{82}$,⁸ $La_2@I_h-C_{80}$,⁹ $Ce_2@D_{3h}-C_{78}$,¹⁰ and $M_2@D_2(10611)-C_{72}$ ($M = La^{11}$ or Ce^{12})] have been isolated and structurally characterized. For carbide-containing endohedrals, three isomers of $M_2C_2@C_{82}$ ($M = Sc, Y$) with different cage geometries— C_s , C_{2v} , and C_{3v} —have been separated and characterized by ¹³C NMR spectroscopy.¹³ Additional examples of carbide-containing endohedrals include $Sc_2C_2@D_{2d}-C_{84}$ ³ and

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$\text{Sc}_2\text{C}_2@C_{68}$.¹⁴ In these carbides, the M_2C_2 unit within the carbon cage assumes a butterfly shape with the C_2 unit perpendicular to a line drawn between the two metal atoms.

The electronic distribution in carbide-containing endohedral fullerenes may be represented by the ionic model, $(\text{M}_2\text{C}_2)^{4+} @ (\text{C}_{2n})^{4-}$. In this model, the Group 3 or lanthanide metal ions exist in their usual M^{3+} state, while the C_2 unit is considered as an acetylide ion, C_2^{2-} . Thus, four electrons must be transferred to the carbon cage. These electrons will fill the LUMO-1 and LUMO-2 orbitals of the corresponding empty fullerene cage. Poblet and co-workers have examined the abilities of various fullerene cages to accept four electrons in this fashion.¹⁵ They suggested that the most stable tetra-anions would have large (LUMO-3)–(LUMO-2) gaps, and they calculated those gaps for the isolated pentagon rule (IPR) empty cage fullerenes from C_{60} to C_{100} . For $\text{M}_2\text{C}_2@C_{82}$, which they considered as the prototypical metal carbide of this class, they computed a (LUMO-3)–(LUMO-2) gap of 1.09 eV for the empty $\text{C}_{3v}(8)\text{-C}_{82}$ cage. For the empty C_{92} cage, which is relevant to the work reported here, they calculated that the $D_3(85)$ isomer had the largest gap, 0.86 eV, with the $\text{C}_1(67)$ isomer having the next largest gap, 0.84 eV.

Gadolinium-containing endohedral fullerenes are particularly important, since they may contribute to the development of a second generation of relaxation agents for magnetic resonance imaging (MRI).¹⁶ A number of gadolinium-containing endohedral fullerenes have already been reported. Both $\text{Gd}@C_{82}$ ¹⁷ and $\text{Gd}@C_{60}$ ¹⁸ have been isolated and functionalized to produce water-soluble forms that are effective for MRI relaxation. Particular attention has been given to the $\text{Gd}_3\text{N}@C_{2n}$ family of endohedrals, since these put three of the paramagnetic centers together in a relatively small, confined space.^{19,20} The structures of three members of that family have been determined by single-crystal X-ray diffraction. These three molecules are $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$, which obeys the IPR and contains a pyramidalized Gd_3N unit,¹⁹ and $\text{Gd}_3\text{N}@C_{3v}(663)\text{-C}_{82}$ ²¹ and $\text{Gd}_3\text{N}@C_{3v}(51365)\text{-C}_{84}$,²² which contain planar Gd_3N units in carbon cages that do not follow the IPR rule. Here, we report the detection of a long series of di-gadolinium endohedrals that extends from Gd_2C_{90} to $\text{Gd}_2\text{C}_{124}$ and report a structural study of one member of a series.

Results

Detection of the Gd_2C_{2n} ($2n = 90\text{--}124$) Family of Endohedral Fullerenes. Carbon soot containing gadolinium endohedral fullerenes was produced by a conventional direct current arc process with a current of 60 A under an atmosphere of 150

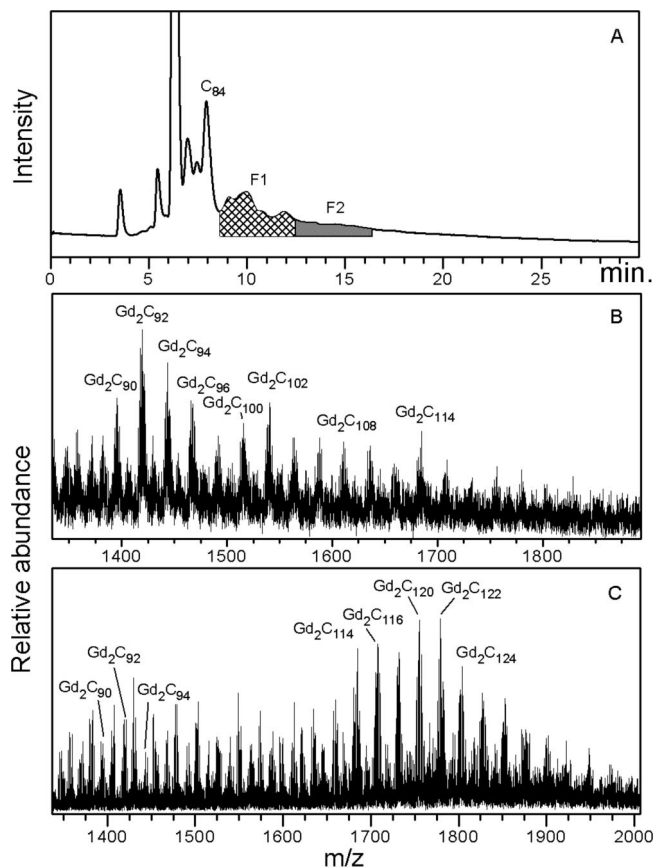


Figure 1. (A) Chromatogram from the initial HPLC of extract on a Buckyprep-M column (mobile phase, chlorobenzene; flow rate, 4 mL/min; detection wavelength, 400 nm). (B) LD-TOF mass spectrum obtained from fraction F1. (C) LD-TOF mass spectrum obtained from fraction F2.

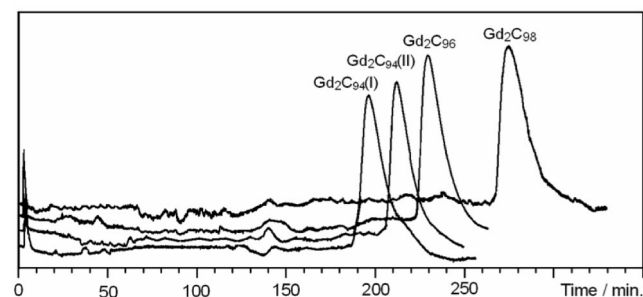


Figure 2. Chromatograms obtained from purified samples of $\text{Gd}_2\text{C}_{94}(\text{I})$, $\text{Gd}_2\text{C}_{94}(\text{II})$, Gd_2C_{96} , and Gd_2C_{98} .

Torr helium. Graphite rods (6×150 mm) that had been core drilled and filled with a mixture of Gd_2O_3 and graphite powder in a 1:70 atomic ratio were used as the anode. The raw soot was dissolved in *o*-dichlorobenzene with sonication for 8 h. Part A of Figure 1 shows the first stage of chromatographic separation of the soluble extracts. Two broad fractions (F1 and F2) were collected, as shown in Figure 1B,C. Mass spectrometric analysis of the soluble material in fraction F1 revealed the presence of a series of di-gadolinium endohedrals extending from Gd_2C_{90} to $\text{Gd}_2\text{C}_{114}$, with Gd_2C_{92} and Gd_2C_{94} as the most prevalent of these, as shown in part B of Figure 1. Fraction F2 was also examined by mass spectrometry and shown to contain di-gadolinium endohedrals as large as $\text{Gd}_2\text{C}_{124}$, as shown in part C of Figure 1. The mass spectrum also contains peaks with larger masses than $\text{Gd}_2\text{C}_{124}$. We have not labeled these higher

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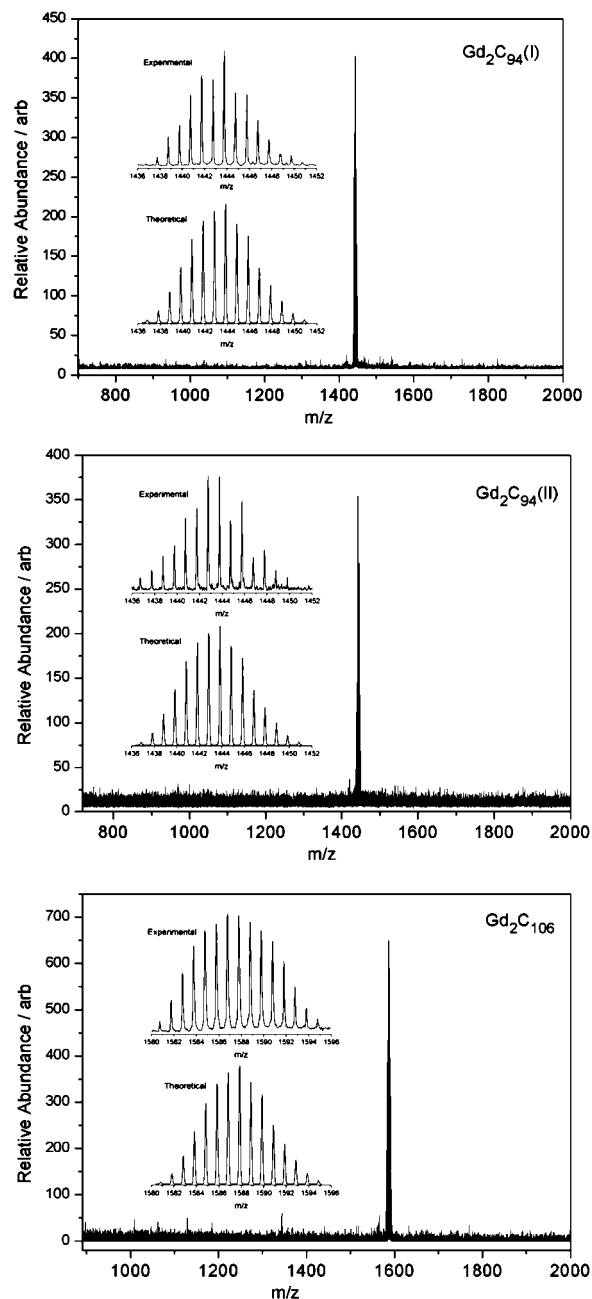


Figure 3. LD-TOF mass spectra obtained from purified samples of isomers $Gd_2C_{94}(I)$ and $Gd_2C_{94}(II)$ and for Gd_2C_{106} . The insets show expansions of the experimental and theoretical spectra for the parent ions.

mass peaks, since the signal-to-noise ratio for such low-intensity peaks did not allow us to make satisfactory comparisons of the computed and observed spectra.

The soluble material in fractions F1 and F2 was subjected to three stages of high-pressure liquid chromatography (HPLC) to obtain the individual endohedrals. The first stage utilized a Buckyprep-M column with chlorobenzene as the eluent, the second stage used a Buckyprep column with toluene as eluent, and the third stage employed a 5PBB column with toluene or xylene as the mobile phase. A fourth stage utilizing a Buckyprep-M column with toluene as eluent was needed to obtain pure samples of Gd_2C_{100} to Gd_2C_{106} . These procedures allowed us to isolate purified samples of the endohedrals from Gd_2C_{94} to Gd_2C_{106} . The chromatograms for purified samples of two isomers of Gd_2C_{94} [the initially eluting $Gd_2C_{94}(I)$ and the more

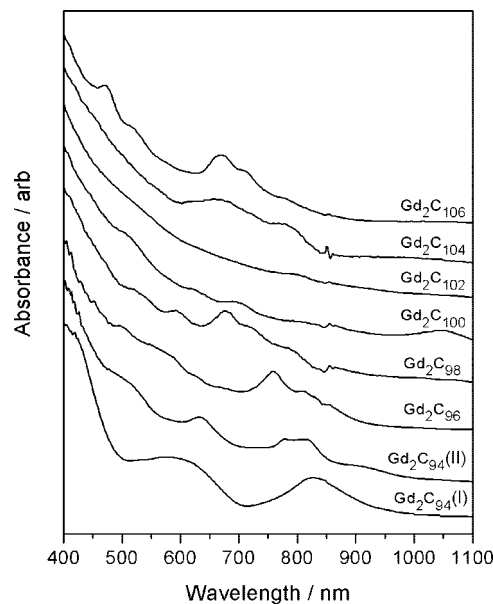


Figure 4. Absorption spectra of Gd_2C_{94} to Gd_2C_{96} in toluene solution and Gd_2C_{98} to Gd_2C_{106} in chlorobenzene solution.

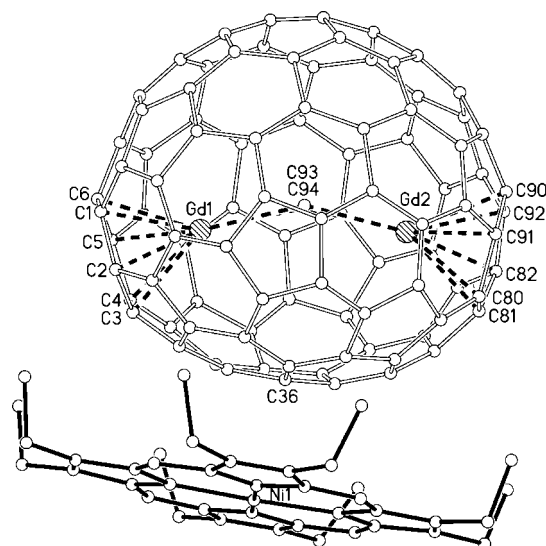


Figure 5. View of the disposition of $Gd_2C_2@D_3(85)-C_{92}$ with respect to the host Ni(OEP) molecule. The three-fold axis of the D_3-C_{92} cage is drawn such that it is horizontal and in the plane of the page. Only one of the two statistically predominant Gd orientations is shown. In the Ni(OEP) portion, the nickel ion is labeled, the four circles attached to nickel are nitrogen atoms, and the other open circles represent carbon atoms. Benzene molecules and hydrogen atoms were omitted for clarity.

slowly eluting $Gd_2C_{94}(II)$], Gd_2C_{96} , and Gd_2C_{98} are shown in Figure 2. Mass spectra for the purified samples of $Gd_2C_{94}(I)$, $Gd_2C_{94}(II)$ and Gd_2C_{106} are shown in Figure 3. $Gd_2C_{94}(I)$ was the first member of this series to produce crystals suitable for X-ray diffraction. Chromatographic and mass spectral data for samples of the family from Gd_2C_{96} to Gd_2C_{106} are given in the Supporting Information.

Figure 4 presents the UV/vis/NIR absorption spectra of both isomers of Gd_2C_{94} along with the spectra of Gd_2C_{96} to Gd_2C_{106} . The spectra show significant variations, as expected, since the

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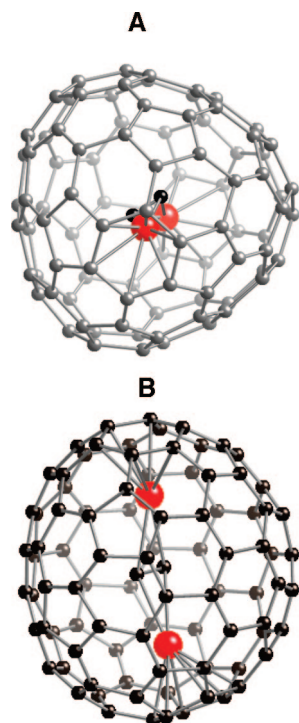


Figure 6. Two orthogonal views of $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$ with cage carbon atoms in gray, the carbide carbon atoms in black, and the gadolinium atoms in red. (A) A view down the non-crystallographic three-fold axis of the carbon cage. (B) A side view with the three-fold axis in the vertical direction. Only the major Gd sites are shown.

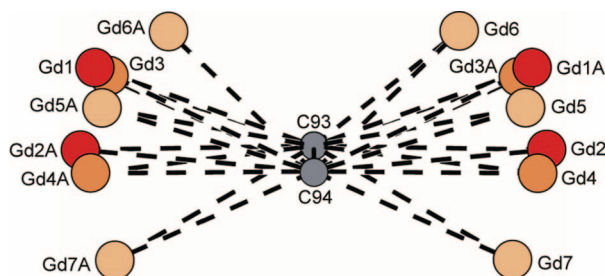


Figure 7. Drawing showing the positions of the gadolinium sites relative to the C_2 unit in $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$. The gadolinium site occupancies are as follow: Gd1, 0.28; Gd2, 0.28; Gd3, 0.16; Gd4, 0.16; Gd5, 0.06; Gd6, 0.04; Gd7, 0.02.

absorptions of endohedral fullerenes are dependent on the cage size and cage geometry. For example, the spectrum of $\text{Gd}_2\text{C}_{102}$ shows a rather featureless increase in absorbance as one moves from low to high energy. In contrast, the spectrum of Gd_2C_{98} shows five clear maxima. The spectra of Gd_2C_{96} and $\text{Gd}_2\text{C}_{100}$ show some very low energy absorptions in the 1000–1100 nm range.

Structure of $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$ As Determined by Single-Crystal X-ray Diffraction. Crystals for X-ray diffraction were obtained by slow diffusion of a benzene solution of $\text{Ni}^{\text{II}}(\text{OEP})$ into a benzene solution of the purified endohedral. Figure 5 shows the structure of the endohedral fullerene and its relationship to the nickel porphyrin. The structural results indicate that Gd_2C_{94} contains a Gd_2C_2 unit inside a cage of 92 carbon atoms. For C_{92} there are 86 isomers that obey the IPR.²³ Four of these have D_3 symmetry.

The fullerene cage in Gd_2C_{94} obeys the IPR and has been identified as $D_3(85)\text{-C}_{92}$.²³ The cage is disordered with the two

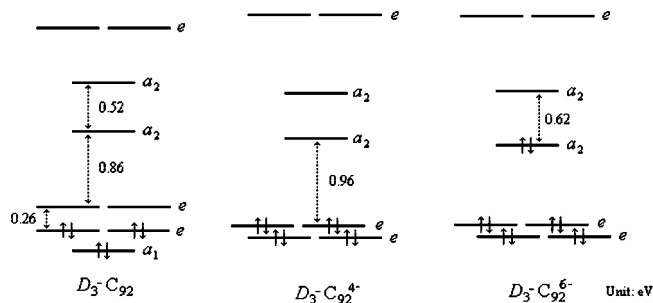


Figure 8. Molecular orbital energy levels for empty cage $D_3(85)\text{-C}_{92}$ as a neutral molecule, tetra-anion, and hexa-anion.

enantiomers of the D_3 -symmetric cage residing at a common site that is bisected by a crystallographic mirror plane. The carbide unit is situated on that crystallographic mirror plane and is ordered with a $\text{C}_{93}\text{-C}_{94}$ distance of 1.04(2) Å.

Figure 6 shows two orthogonal views of $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$. The fullerene cage is elongated along the three-fold axis. C_1 and C_{92} , which lie along the three-fold axis, are 9.43(4) Å apart. The three perpendicular two-fold axes pass through the centers of C–C bonds, and the corresponding cage dimensions are 8.32, 8.32, and 8.34 Å.

There are seven sites for gadolinium ions with occupancies 0.28 for Gd1 and Gd2, 0.16 for Gd3 and Gd4, 0.06 for Gd5, 0.04 for Gd6, and 0.02 for Gd7. Figure 7 shows how these seven gadolinium sites and the seven corresponding sites generated by reflection are arranged about the C_2 unit. The number of gadolinium sites suggests that the metal atoms are free to move about the C_2 unit and about the inner surface of the fullerene. While it appears that the Gd_2C_2 unit has a butterfly shape, the dihedral angle between the two Gd_2C portions seems to be flexible. Other examples of M_2C_2 units in fullerene cages also have been shown to have a butterfly shape.^{3,4} The prominent gadolinium sites reside near the C_3 axis at the ends of the cage as seen in Figure 6. For the carbide moiety, the Gd–C distances for the two most populated sites fall in the range 2.484(7)–2.527(5) Å. These gadolinium sites are located near the centers of hexagons on the inside of the fullerene cage. Such positioning near hexagons is common for other large lanthanide atoms inside fullerene cages.^{24,25}

Computational Studies of the Electronic Structure of $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$ and Related Molecules

Figure 8 shows the molecular orbital energies computed for the neutral, tetra-anionic, and hexa-anionic forms of $D_3(85)\text{-C}_{92}$ using DFT methodology at the B3LYP level. The additional four electrons are accommodated by the LUMO e level, and the e to a_2 gap increases to 0.96 eV in the tetra-anion.

However, the structure of isomer II of Gd_2C_{94} remains to be established. This isomer could also have the carbide structure, $\text{M}_2\text{C}_2@C_{92}$, with a different cage geometry. In this case, the $\text{C}_1(67)\text{-C}_{92}$ cage appears to be a likely candidate due to the relatively large (LUMO-3)–(LUMO-2) gap.¹⁵ Alternately, isomer II of Gd_2C_{94} could have the conventional $\text{M}_2@C_{94}$ structure. In that case, the $\text{M}_2@C_2(121)\text{-C}_{94}$ isomer is the one computed to be the most stable according to the study of Popov and Dunsch.²⁶

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Computations were also performed to compare the relative stabilities of the carbide, $\text{Gd}_2\text{C}_2@C_{92}$, and the conventional endohedral, $\text{Gd}_2@C_{94}$. For the former, we used the experimentally determined structure, $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$. For the latter, we initially examined $\text{Gd}_2@C_2(121)-C_{94}$, since Popov and Dunsch had previously computed that the $C_2(121)-C_{94}$ cage was the most stable C_{94} cage in the hexa-anion form.²⁶ Computations performed at the B3LYP level with the 3-21G(d) basis set showed that $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$ was more stable than $\text{Gd}_2@C_2(121)-C_{94}$ by 3.88 kcal/mol in total energy. The HOMO–LUMO gap in $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$ was computed to be 1.762 eV, while this gap was only 0.902 eV in $\text{Gd}_2@C_2(121)-C_{94}$. Additional computations were performed for $\text{Gd}_2\text{C}_2@C_2(64)-C_{92}$ and $\text{Gd}_2\text{C}_2@C_1(67)-C_{92}$. Relative to $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$, these had higher energies: 6.61 kcal/mol for $\text{Gd}_2\text{C}_2@C_2(64)-C_{92}$ and 8.15 kcal/mol for $\text{Gd}_2\text{C}_2@C_1(67)-C_{92}$. Thus, the calculations confirm the high stability of $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$ and suggest that isomer II of Gd_2C_{94} may be $\text{Gd}_2@C_2(121)-C_{94}$. The idea that isomer II of Gd_2C_{94} may be $\text{Gd}_2@C_2(121)-C_{94}$ is also consistent with the chromatographic behavior of the two Gd_2C_{94} isomers. As seen in Figure 2, the observed retention time for isomer II of Gd_2C_{94} is indicative of the presence of a 94-atom carbon cage.

Discussion

This work has demonstrated that an extensive series of large di-gadolinium endohedral fullerenes – Gd_2C_{90} to $\text{Gd}_2\text{C}_{124}$ – exists and has shown that examples as large as $\text{Gd}_2\text{C}_{106}$ can be isolated in sufficient quantities to allow physical characterization. To our knowledge, $\text{Gd}_2\text{C}_{106}$ is the largest endohedral fullerene yet isolated. For Gd_2C_{94} , two isomers have been found and separated. One is clearly the carbide, $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$, while the other is likely to be a conventional endohedral, $\text{Gd}_2@C_2(121)-C_{94}$. Related families of di-erbium and di-dysprosium endohedrals have been reported previously, but these families do not extend to the large sizes reported here. With erbium, Shinohara and co-workers isolated three isomers of Er_2C_{86} , Er_2C_{88} , and $\text{Er}_2@C_{90}$, four isomers of Er_2C_{92} , and two isomers of Er_2C_{94} .²⁷ With dysprosium, Yang and Dunsch have isolated two isomers of Dy_2C_{94} and $\text{Dy}_2\text{C}_{100}$.²⁸

The absorption spectrum of $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$ in the UV/vis/NIR regions, shown in Figure 4, exhibits prominent absorp-

tion maxima at 820 and 590 nm. The corresponding spectra previously reported for the initially eluting isomers I of Er_2C_{94} ²⁷ and Dy_2C_{94} ²⁸ are quite similar. Since the electronic spectra of endohedral fullerenes generally depend more on the cage geometry than on the cage contents, the similarities suggest that these endohedrals may have the structures $\text{Dy}_2\text{C}_2@D_3(85)-C_{92}$ and $\text{Er}_2\text{C}_2@D_3(85)-C_{92}$. Likewise, the absorption spectra of the more slowly eluting isomers II of Er_2C_{94} ²⁷ and Dy_2C_{94} ²⁸ are similar to the absorption spectrum of isomer II of Gd_2C_{94} , and again these three molecules may share a common structure, probably $\text{M}_2@C_2(121)-C_{94}$ as suggested by the computational studies.

As noted earlier, the electronic distribution in carbide-containing endohedral fullerenes may be represented by the ionic model, $(\text{M}_2\text{C}_2)^{4+}@(C_{2n})^{4-}$, in which four electrons are transferred to the fullerene cage. These electrons will fill the LUMO-1 and LUMO-2. Consequently, the most stable tetra-anions should have large (LUMO-3)–(LUMO-2) gaps. For C_{92} , Poblet and co-workers calculated that the $D_3(85)$ isomer had the largest gap, 0.86 eV, with the $C_1(67)$ isomer having the next largest gap, 0.84 eV.¹⁵ Our observation that isomer I of Gd_2C_{94} is $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}$ offers validation of the utility of the (LUMO-3)–(LUMO-2) rule of Poblet and co-workers.

Identifying the structures of the other new di-gadolinium endohedrals reported here will require further work, since these compounds may exist as either the conventional endohedral, $\text{M}_2@C_{2n}$, or the carbide, $\text{M}_2\text{C}_2@C_{2n-2}$.

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Supporting Information Available: Experimental section, HPLC chromatograms and MS spectra of the purified samples of Gd_2C_{96} to Gd_2C_{94} ; X-ray crystallographic files in CIF format for $\text{Gd}_2\text{C}_2@D_3(85)-C_{92}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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