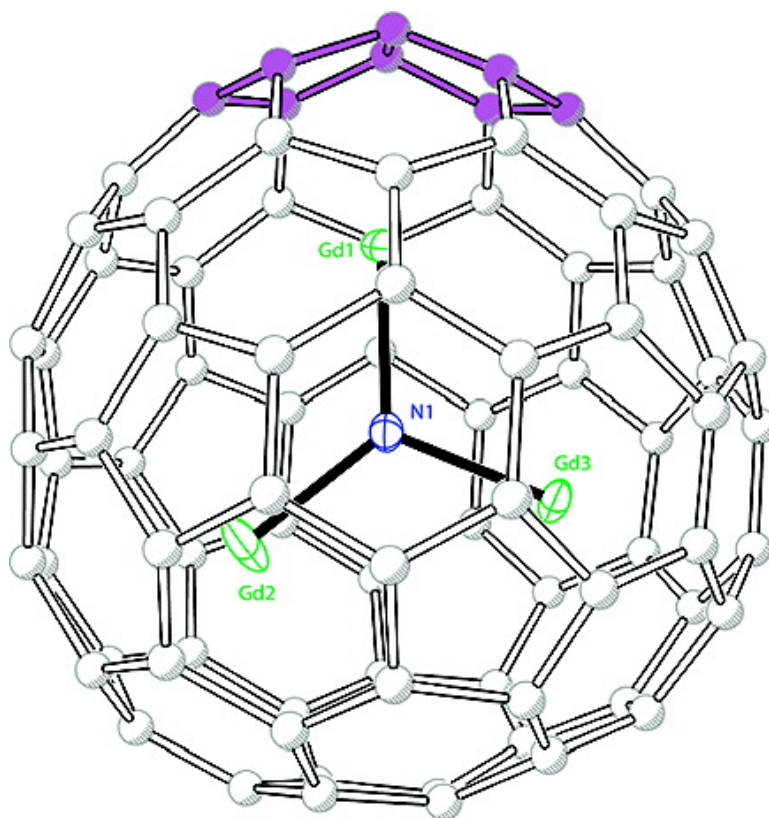


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Is the Isolated Pentagon Rule Merely a Suggestion for Endohedral Fullerenes? The Structure of a Second Egg-Shaped Endohedral Fullerene—Gd₃N@C_s(39663)-C₈₂

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The C₈₂ cage has played an important role in the development of endohedral fullerene chemistry. In 1991 Smalley and co-workers observed that La@C₈₂, unlike La@C₆₀ and La@C₇₄, had good solubility in organic solvents and high stability.¹ Subsequently, endohedral fullerenes with C₈₂ cages have become particularly numerous and have been subject to external modification through addition reactions.² Nine isomers (three C₂ isomers, three C_s isomers, two C_{3v} isomers, and one C_{2v} isomer) of the C₈₂ cage obey the isolated pentagon rule (IPR), which requires that each of the twelve pentagons in a fullerene be surrounded by hexagons.³ It has been established that the major and minor isomers of La@C₈₂ have IPR-obeying cage structures with C_{2v}⁴ and C_s⁵ symmetry, respectively, and the C_{2v} structure appears to be established for a number of other endohedrals of the M@C₈₂ type (M = Y, Ca, etc.).⁶ The structures of two of the three known isomers of Er₂@C₈₂ have been crystallographically characterized and shown to have IPR-obeying structures Er₂@C_s(6)-C₈₂⁷ and Er₂@C_{3v}(8)-C₈₂.⁸

Endohedral fullerenes containing the trimetallic nitride (TN) M₃N unit are particularly important because they can be obtained in unusually high yields.⁹ While the structures of several TN endohedral fullerenes have been reported,^{9–13} no structural data for M₃N@C₈₂ have been available. Poblet and co-workers have predicted that M₃N@C₈₂ will not obey the IPR because of the lack of an appropriately large gap in the molecular orbital energies in the hexa-anion of the empty cage.¹⁴ Computational studies by Popov and Dunsch suggested that the structures M₃N@C_{2v}(39705)-C₈₂ and M₃N@C_s(39663)-C₈₂ are the most probable isomers for the C₈₂ TN endohedrals.¹⁵

A sample of Gd₃N@C_s(39663)-C₈₂ was prepared in an electric arc-discharge reactor by vaporizing graphite rods containing a mixture of Gd₂O₃ and graphite powder in a ~400 Torr He/N₂ atmosphere as outlined previously.¹⁶ The xylene extract from the raw soot was passed through a cyclopentadiene-functionalized Merrifield peptide resin to remove the empty-cage fullerenes. The higher order species were separated via HPLC. The third fraction contained Gd₃N@C_s(39663)-C₈₂.¹⁶ The HPLC chromatogram, negative ion MALDI-TOF MS spectrum, and the UV-vis absorption spectrum of the Gd₃N@C_s(39663)-C₈₂ are reproduced in the Supporting Information.

Black parallelepipeds of Gd₃N@C_s(39663)-C₈₂·Ni^{II}(OEP)·2(C₆H₆) were obtained by diffusion of a benzene solution of the endohedral fullerene into a benzene solution of Ni^{II}(OEP) and utilized in the crystal structure determination.¹⁷

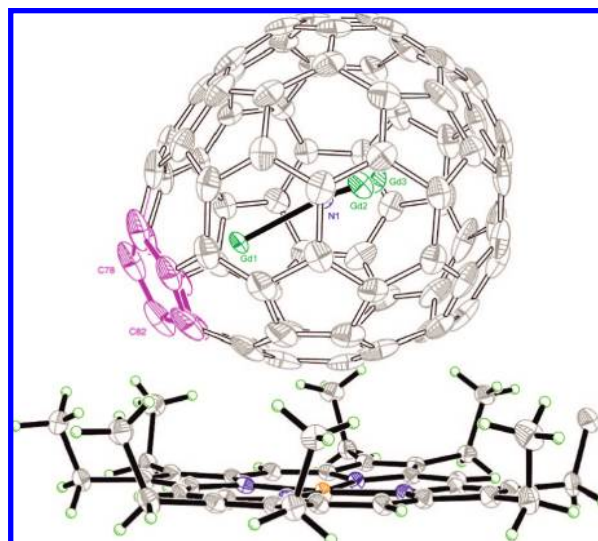


Figure 1. A view of the structure of Gd₃N@C_s(39663)-C₈₂·Ni^{II}(OEP)·2C₆H₆ with 30% thermal contours. The pair of fused pentagons is highlighted in purple. Only the major site for the Gd₃ group is shown. For clarity, the solvated molecules of benzene have been omitted.

Figure 1 shows a drawing of the egg-shaped Gd₃N@C_s(39663)-C₈₂ molecule, which is nestled within the eight ethyl groups of the Ni^{II}(OEP) molecule. The carbon cage in Gd₃N@C_s(39663)-C₈₂ does not obey the isolated pentagon rule. The ring spiral for this carbon cage is 1, 2, 11, 13, 17, 19, 26, 31, 33, 35, 38, 43. The one fused pentagon pair is highlighted in Figure 1 in purple. For a C₈₂ there are the 9 isomers that conform to the IPR and 39709 isomeric structures that do not conform to the IPR if only pentagons and hexagons are found within the carbon framework.³ The structure found here is one of the two previously predicted to be stable for a C₈₂ cage bearing a 6⁻ charge.¹⁵

The fullerene cage in Gd₃N@C_s(39663)-C₈₂ closely resembles the cage found for the most prevalent isomer of M₃N@C₈₄, which is M₃N@C_s(51365)-C₈₄ (M = Gd, Tb, Tm).^{18,19} A comparison of the shapes of these two fullerenes is presented in Figure 2. Both cages have an egg shape with mirror symmetry and a single location where two pentagons abut. In both cases the mirror plane of the fullerene is positioned perpendicular to the C–C bond that connects the two pentagonal rings.

There is some disorder in the structure. Gd1, Gd2, and Gd3 constitute the major site for this group with 0.84, 0.67, and 0.70 fractional occupancy, respectively. The Gd–N distances are 2.152(5), 2.094(5), and 2.077(5) Å for Gd1, Gd2, and Gd3,

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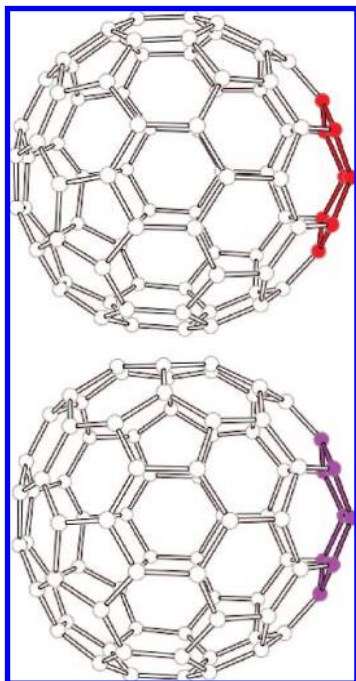


Figure 2. A comparison of the structures of the fullerene cages in $Gd_3N@C_s(39663)-C_{82}$ (bottom with the fused pentagon pair highlighted in purple) and $Gd_3N@C_s(51365)-C_{84}$ (top with the fused pentagon pair highlighted in red). The noncrystallographic mirror plane in each case lies parallel to the page.

respectively. The Gd_3N unit is planar at the major site. The sum of the three $Gd-N-Gd$ angles is 359.6° . There are an additional 16 Gd sites with occupancies ranging from 0.09 to 0.02. The carbon cage also displays disorder with two orientations for the cage.

Gd1 is situated within the fold of the pentalene unit formed by the fused pentagon pair. Within that unit the $Gd-C$ distances are shortest at the fold ($Gd1-C78$, 2.476(10), $Gd1-C82$, 2.484(10) Å) and longer for the four adjacent carbon atoms, which range from 2.486(9) to 2.554(10) Å. The $Gd1-C78$ and $Gd1-C82$ distances are comparable to the $Gd-C$ distances (2.470(15) and 2.479(16)) in $Gd_3N@C_s(51365)-C_{84}$.¹⁹ The positioning of Gd1 near the fused pentagon pair is similar to that of the Gd, Tb, and Tm ions in $M_3N@C_s(51365)-C_{84}$ and the Sc ions within the three pentalene units of $Sc_3N@D_{3h}(6140)-C_{68}$.^{11,18,19} For comparison, there is a significant body of data available for coordination of organometallic groups to the inner face of pentalene and substituted pentalenes.²⁰

Within the family of TN fullerenes, crystallographic data show that $Sc_3N@D_{3h}(5)-C_{78}$,¹⁰ $M_3N@I_h-C_{80}$ ($M = Sc, Gd, Tb$),^{9,13} $M_3N@D_{5h}-C_{80}$ ($M = Sc, Tb$),^{12,13} $Tb_3N@D_3-C_{86}$,¹³ and $Tb_3N@D_2(35)-C_{88}$ ¹³ obey the IPR, but $Sc_3N@D_3(6140)-C_{68}$,¹¹ $Gd_3N@C_s(39663)-C_{82}$, and $M_3N@C_s(51365)-C_{84}$ ($M = Gd, Tb, Tm$)^{18,19} do not. Additional exceptions to the IPR rule that have been reported include: $Sc_3N@C_{2v}(7854)-C_{70}$,²¹ $DySc_2N@C_s(17490)C_{76}$,²² $Sc_2@C_{66}$,²³ $Sc_2C_2@C_{2v}(6073)-C_{68}$,²⁴ $La_2@D_2(10611)-C_{72}$,²⁵ and $La@C_{72}$.²⁶ With this growing list of exceptions, the IPR indeed appears to be more a suggestion than a rule for endohedral fullerenes.

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Supporting Information Available: Complete ref. 4a; preparative and separation information for $Gd_3N@C_s(39663)-C_{82}$; X-ray crystallographic data for $Gd_3N@C_s(39663)-C_{82}\cdot Ni^{II}(OEP)\cdot 2(C_6H_6)$ in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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