

New egg-shaped fullerenes: non-isolated pentagon structures of $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ and $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}^{\dagger\dagger}$

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Received (in Berkeley, CA, USA) 17th October 2007, Accepted 21st December 2007

First published as an Advance Article on the web 31st January 2008

DOI: 10.1039/b716037b

Although there are 51 568 non-IPR and 24 IPR structures for C_{84} , the egg-shaped endohedral fullerenes $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ and $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ utilize the same non-IPR cage structure as found initially for $\text{Tb}_3\text{N}@C_s(51\,365)\text{-C}_{84}$.

Most fullerenes and endohedral fullerenes obey the isolated pentagon rule (IPR) which minimizes the steric strain in the carbon cage by placing five hexagons about each pentagon, thus eliminating any direct pentagon–pentagon contact.¹ In 1999 a new family of endohedral fullerenes was discovered that contained the $(\text{M}_3\text{N})^{6+}$ unit,² and further related families have continued to be prepared.^{3,4} These endohedral fullerenes were obtained by conducting the Krätschmer–Huffman electric arc synthesis from graphite and a suitable metal oxide in the presence of dinitrogen. This discovery made endohedrals of the $\text{M}_3\text{N}@C_{2n}$ type available in sufficient quantity for extensive physical and chemical characterization. In 2005 Poblet and co-workers utilized electronic structure computations on empty fullerenes to examine the cage structures most suitable for encapsulating $(\text{M}_3\text{N})^{6+}$ units and predicted that, among others, none of the IPR structures of C_{84} would be suitable.⁵ The structure of $\text{Tb}_3\text{N}@C_s(51\,365)\text{-C}_{84}$,^{6,7} the more abundant and second eluting of the two isomers of $\text{Tb}_3\text{N}@C_{84}$, was determined in 2006 and found to violate the IPR.⁸ While there are 24 IPR isomeric structures available for a C_{84} cage, the second eluting isomer of $\text{Tb}_3\text{N}@C_{84}$ adopts one of the 51 568 isomeric structures that do not conform to the IPR. It utilizes non-IPR structure no. 51 365 with C_s symmetry and the ring spiral code: 1 2 11 13 16 18 29 31 33 35 37 44.¹ This cage has a single site where two pentagons abut. With such a large number of isomeric

C_{84} cages as possible hosts for $(\text{M}_3\text{N})^{6+}$ units, it remained to be determined whether other metals would utilize the same cage structure in forming analogs of $\text{Tb}_3\text{N}@C_s(51\,365)\text{-C}_{84}$. Here we report the isolation and structures of one of the isomers of $\text{Tm}_3\text{N}@C_{84}$ and one of the isomers of $\text{Gd}_3\text{N}@C_{84}$.

A sample of $\text{Tm}_3\text{N}@C_{84}$ was synthesized in an arc-discharge generator by vaporizing composite graphite rods packed with a mixture of Tm_2O_3 , graphite powder and Fe_xN in a weight ratio of 2.09 : 1.0 : 0.4 respectively, under a static, low pressure He– N_2 atmosphere (280 torr He and 20 torr N_2). The raw soot was extracted for 20 h with toluene in a Soxhlet device. After chemical separation using a cyclopentadiene-functionalized Merrifield peptide resin,⁹ the sample was injected onto an HPLC with a 5PBB column. The eluent produced seven thulium-containing fractions. The fourth fraction contains two isomers of $\text{Tm}_3\text{N}@C_{84}$ (I, II) and two isomers of $\text{Tm}@C_{90}$ (I, II). The first eluting isomer, $\text{Tm}_3\text{N}@C_{84}$ (I), is much less abundant than the second isomer. The structural work reported here was done on the second and more abundant isomer, $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$, isolated in the second HPLC stage using a 5PYE column. The HPLC chromatogram, negative-ion LD-TOF (laser-desorption time-of-flight) MS spectrum, and the UV–Vis

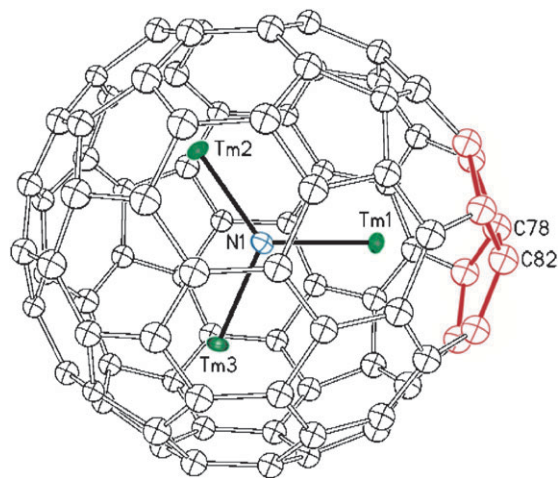


Fig. 1 A view of the $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ molecule in the structure of $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}\text{-Ni(OEP)}\cdot 2\text{C}_6\text{H}_6$ with 30% thermal contours. The molecule is oriented so that the Tm_3N unit is parallel to the plane of the page. The pair of fused pentagons is highlighted in red. Only the major site for the Tm_3 group is shown.

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† CCDC 664500 & 664501. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716037b

‡ Electronic supplementary information (ESI) available: Experimental details and crystallographic data in cif format. See DOI: 10.1039/b716037b

absorption spectrum of the pure $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ are shown in the supporting information.†

A sample of $\text{Gd}_3\text{N}@C_{84}$ was obtained by vaporizing graphite rods containing a mixture of Gd_2O_3 and graphite powder in a ~ 400 Torr He– N_2 atmosphere. The raw soot was extracted for ~ 20 h with xylene. The extract was treated with a cyclopentadiene-functionalized Merrifield peptide resin to remove the empty-cage fullerenes, and the higher order species were separated from the $\text{Gd}_3\text{N}@C_{80}$ via HPLC as described previously.^{10,11} Three isomers of $\text{Gd}_3\text{N}@C_{84}$ were separated using a Buckyprep-M column. The HPLC chromatogram and the MALDI-TOF MS spectrum of the purified sample of $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}$, which is the first eluting and most abundant of the three $\text{Gd}_3\text{N}@C_{84}$ isomers, are given in the supporting information.‡

Black parallelepipeds of $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ and black blocks of $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ were obtained by diffusion of a benzene solution of the appropriate endohedral fullerene into a benzene solution of $\text{Ni}^{\text{II}}(\text{OEP})$ and utilized for the crystal structure determinations by X-ray diffraction.§ The two crystals are isostructural. Fig. 1 shows a drawing of the $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ molecule in $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ from a perspective that looks down on the plane of the Tm_3N unit. The fullerene cage does not obey the IPR; there is one pentagon–pentagon contact, which is highlighted in red. Fig. 2 shows the positioning of the $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ molecule relative to the $\text{Ni}^{\text{II}}(\text{OEP})$ molecule in $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$. Again the two adjoining pentagons are colored red.

The fullerene cages in $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ and $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ have the same C_s structure and utilize the same cage isomer (non-IPR isomer no. 51 365 with ring spiral code: 1 2 11 13 16 18 29 31 33 35 37 44)¹ as found originally in $\text{Tb}_3\text{N}@C_s(51\,365)\text{-C}_{84}$.⁸ It is also important to realize that the same non-IPR cage is formed under different experimental conditions utilizing three different metal oxide precursors, different packing materials inside the graphite rods and different arc-discharge generators. The occurrence of the same cage structure in these three different molecules suggests that it is the carbon cage and the number of electrons transferred to it by the metals inside, rather than the specific metals trapped inside, that determine which of the multitude of structures available for a cage of 84 carbon atoms is actually utilized, as noted in recent computational studies.^{5,12} The carbon atoms in $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ and $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ display the same type of cage disorder as previously found for $\text{Tb}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$. The 64 atoms of the cage closest to the fused pentagon pair are well behaved, but the 20 carbon atoms at the opposite end are found in two sets of positions that are related by a 180° rotation of the cage.

The metal ions inside the cages also display disorder. For $\text{Tm}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ the major sites involved Tm1 with 0.90 occupancy as well as Tm2 and Tm3, each with occupancy of 0.38. Sites Tm4 and Tm5 have 0.23 occupancy, sites Tm6 and Tm7 have 0.25 occupancy and sites Tm8 and Tm9 have 0.04 occupancy. Tm10, which is near Tm1, is the only detected component of a minor Tm_3N orientation. In $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ the major sites involved Gd1 with 0.85 occupancy, Gd2 with occupancy of 0.38 and Gd3 with occupancy of 0.51. There are eight other Gd sites with

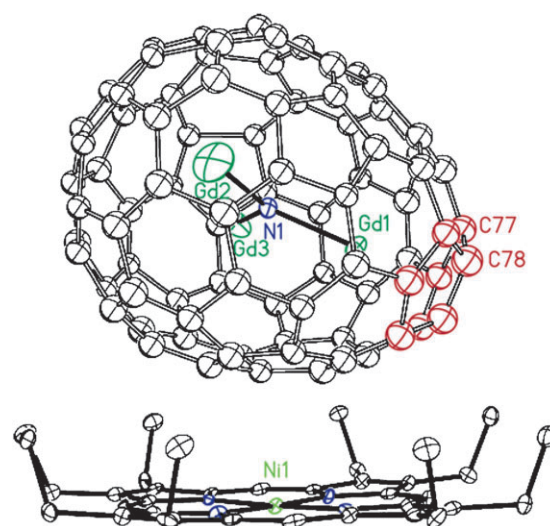


Fig. 2 A view of the structure of $\text{Gd}_3\text{N}@C_s(51\,365)\text{-C}_{84}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ with 30% thermal contours. The pair of fused pentagons is highlighted in red. Only the major sites for the Gd_3 group are shown. For clarity, the solvate molecules of benzene have been omitted.

occupancies ranging from 0.29 to 0.05. In the major sites the Tm_3N and Gd_3N units are planar. In both cases the sum of the three M–N–M angles is 359.7° . Fig. 3 shows the dimensions of the M_3N units in the three $\text{M}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ and the interactions between one of the metal atoms of the M_3N unit with carbon atoms of the pair of abutting pentagons. In all three cases the M–N distances and the M–C distances are similar.

A significant number of violations of the IPR now exist among the numerous endohedral fullerenes that have been prepared. In addition to the $\text{M}_3\text{N}@C_s(51\,365)\text{-C}_{84}$ ($\text{M} = \text{Tb}, \text{Tm}, \text{Gd}$) family discussed here, $\text{La}@C_{72}$ has recently been crystallographically shown to have a non-IPR structure with the La ion also closely associated with the single pair of fused pentagons in the carbon cage.¹³ For such a 72-carbon-atom cage there is only one IPR structure, but computational studies of both empty cage C_{72} and $\text{Ca}@C_{72}$ indicated that non-IPR structures had greater stability than the IPR cage.^{14–16} A study of $\text{La}_2@C_{72}$ by NMR spectroscopy also indicated that $\text{La}_2@C_{72}$ has a non-IPR cage with two pairs of fused pentagons.¹⁷ There are no IPR-obeying structures for C_{66} and C_{68} . Consequently, $\text{Sc}_2@C_{66}$,¹⁸ $\text{Sc}_2\text{C}_2@C_{2v}(6073)\text{-C}_{66}$,¹⁹ and $\text{Sc}_3\text{N}@D_3(6140)\text{-C}_{68}$ ^{20,21} must have non-IPR structures. A crystallographic study of $\text{Sc}_3\text{N}@D_3(6140)\text{-C}_{68}$ shows that the three scandium ions reside near the three fused pentagons.²⁰ Recent computational and spectroscopic studies have suggested that $\text{Sc}_3\text{N}@C_{70}$ also has a non-IPR structure of C_{2v} symmetry with the scandium ions again proximate to three fused pentagon pairs.²² These results highlight the fact that the metal ions in the non-IPR cages are associated with the fused pentagons. Theoretical calculations indicate that the charge transferred from the M_3N cluster to the carbon cage is mainly localized in the fused pentagon moiety.²³ Thus, the antiaromatic fused pentagon moiety becomes more aromatic in character. This charge distribution may explain the experimental observations that fused pentagon pairs are always associated with the presence of a metal ion in the pentalene fold of endohedral fullerenes that do not obey the IPR. It also appears the IPR is

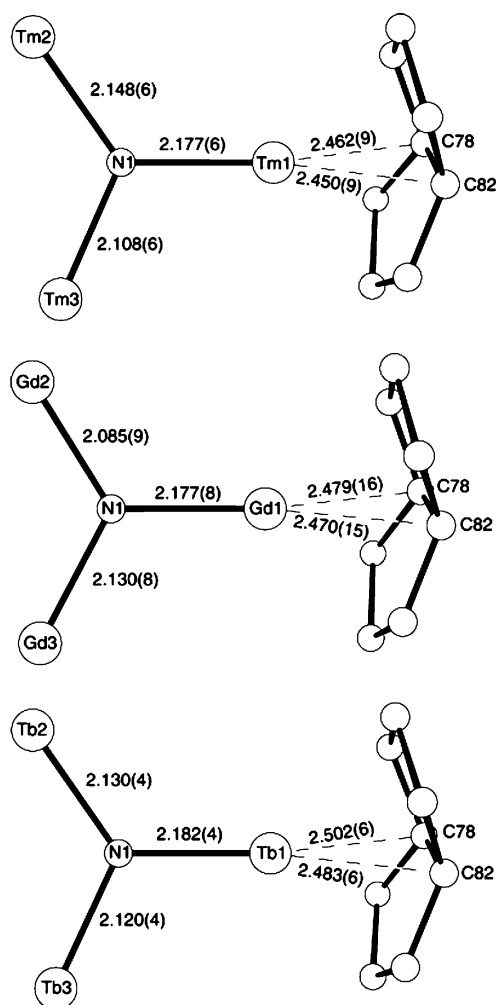


Fig. 3 Views showing the locations of the M₃N units with respect to the fused pair of pentagons in Tm₃N@C₈₄(51 365)-C₈₄, Gd₃N@C₈₄(51 365)-C₈₄ and Tb₃N@C₈₄(51 365)-C₈₄ and some dimensions (in Å) within these units.

not as strong as a predictive tool in endohedral fullerene chemistry as it appears to be for empty cage fullerenes.

In summary, we have determined that the structures of the most abundant isomers of Tm₃N@C₈₄ and Gd₃N@C₈₄ involve a non-IPR cage (no. 51 365) with C_s symmetry and that both are isostructural with Tb₃N@C₈₄(51 365)-C₈₄.⁸ It remains to be determined whether the other isomers of Tm₃N@C₈₄ and Gd₃N@C₈₄ have IPR or non-IPR structures.

We thank the National Science Foundation (Grants CHE-0716843 and CHE-0413857 to ALB, CHE-043700 and DMR-0507083 to HCD, and CHE-0509989 to AJA and LE) and the National Institute of Health (1R01-CA119371-01 to HCD, HWG) for support. This material is also based upon work supported by the AFOSR and Luna Innovations Incorporated under Contract No. FA9550-05-C-0146.

Notes and references

§ Crystal data: Tm₃N@C₈₄(51 365)-Ni(OEP)-2benzene, black parallelepipeds of C₁₃₂H₅₆Tm₃N₅Ni, *M* = 2277.32, triclinic, space group

P $\bar{1}$, *a* = 14.6305(7) Å, *b* = 15.0074(7) Å, *c* = 19.8162(9) Å, α = 85.178(2)°, β = 89.457(2)°, γ = 62.276(2)°, *V* = 3835.7(3) Å³ at 90(2) K, μ (Mo K α) = 3.750 mm, *Z* = 2. Refinement of 17 563 reflections, 995 parameters and 1 restraint yielded *wR*₂ = 0.195 for all data and a conventional *R*₁ = 0.068 based on 13 851 reflections with *I* > 2 σ (*I*). Gd₃N@C₈₄(51 365)-Ni(OEP)-2benzene, black blocks of C₁₃₂H₅₆Gd₃N₅Ni, *M* = 2242.28, triclinic, space group *P* $\bar{1}$, *a* = 14.6344(11) Å, *b* = 15.0158(11) Å, *c* = 19.7975(14) Å, α = 85.319(2)°, β = 89.353(2)°, γ = 62.328(2)°, *V* = 3838.2(5) Å³ at 90(2) K, μ (Mo K α) = 2.872 mm, *Z* = 2. Refinement of 13 632 reflections, 988 parameters and 49 restraints yielded *wR*₂ = 0.261 for all data and a conventional *R*₁ = 0.090 based on 8125 reflections with *I* > 2 σ (*I*).[†]

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- (a) S. Stevenson, C. J. Chancellor, H. M. Lee, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, in press; (b) The symbol Tb₃N@C_s(51 365)-C₈₄ is used here to denote that the Tb₃N unit resides inside a fullerene cage with idealized C_s symmetry. Such a symbolism is needed because endohedrals are known to exist with various cage isomers, e.g. both Sc₃N@I_h-C₈₀ and Sc₃N@D_{5h}-C₈₀ have been isolated, purified and crystallographically characterized.⁷ Consequently, the specific cage isomer should be specified once that information has been obtained. In those cases where more than one cage isomer with a particular cage symmetry exists (as is the case here), further identification is specified by adding, in parenthesis, the number of that isomer from the list given by Fowler and Manolopoulos.¹ For endohedrals that do not obey the isolated pentagon rule, the number of possible cage isomers can be quite large. In general, the overall symmetry of the entire endohedral may be lower than that of the cage individually because of the placement of the atoms on the inside.
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