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$Tb_3N@C_{84}$: An Improbable, Egg-Shaped Endohedral Fullerene that Violates the Isolated Pentagon Rule

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Fullerenes that obey the isolated pentagon rule (IPR) avoid pentagon−pentagon contacts by having each of their 12 pentagons surrounded by 5 hexagons.[1] This arrangement minimizes the steric strain that results from misalignment of the p-orbitals on the fullerene surface. For C_{60} and C_{70}, there is only one way of arranging the pentagons and hexagons to produce an IPR structure, but for higher fullerenes, several isomers can obey the IPR. For example, there are 24 isomeric structures for C_{84} that conform to the IPR. Several isomers of C_{84} have been isolated to date.[2] The most prevalent are the IPR D_{2d}(II) and D_2(IV) isomers. The structure of the D_{2d}(II) isomer has been firmly established through a crystallographic investigation of an adduct with $Ir(CO)Cl(PPh_3)_2$.[3] Minor isomers have been shown to have C_s (two examples), C_2 (two examples), D_2, D_{2d}, D_{3d}, and D_{6h} symmetries though ^{13}C NMR spectroscopic studies.

Well-characterized fullerenes that deviate from the IPR rule are largely confined to endofullerenes, closed carbon cages with atoms inside.[4] Since there are no IPR structures possible for the closed cages of C_{66} and C_{68}, the observation of the existence of the endohedrals $Sc_2@C_{66}$[5] and $Sc_3N@C_{68}$[6] implied that they had non-IPR structures, and structural work has confirmed this. There has been considerable computational work suggesting the endofullerenes of the type $M@C_{72}$ may have non-IPR structures.[7] There is only one IPR isomer possible for C_{72}. The existence of two isomers of $Ca@C_{72}$ suggests that at least one must have a non-IPR structure[8] if the isomerization comes from the cage and not from the location of the metal inside the cage. The ^{13}C NMR spectrum of $La_2@C_{72}$ does not conform to that expected for the one IPR structure with D_{6d} symmetry for this cage size, and two non-IPR structures with two fused pentagon pairs in each have been identified as the likely structures.[9] Here we report isolation and structural characterization of an endohedral C_{84} that does not obey the IPR.

A sample of $Tb_3N@C_{84}$ was synthesized in an arc-discharge generator by vaporizing composite graphite rods containing a mixture of Tb_4O_7, graphite powder, and Fe_xN as catalyst with a weight ratio of 2.03:1.0:0.4, respectively, in a low-pressure He/N_2 atmosphere. The raw soot was extracted for 20 h with toluene in a Soxhlet device. The HPLC of the elution from a cyclopentadiene-functionalized Merrifield peptide resin column produced seven terbium-containing fractions.[10] The fourth fraction contains two isomers of $Tb_3N@C_{84}$. The structural work reported here was done on the second and more abundant of these to elute on a 5PYE column. The HPLC chromatogram, negative ion DCI MS spectrum, and the UV/vis absorption spectrum of the pure isomer 2 of $Tb_3N@C_{84}$ are shown in Figure 1.

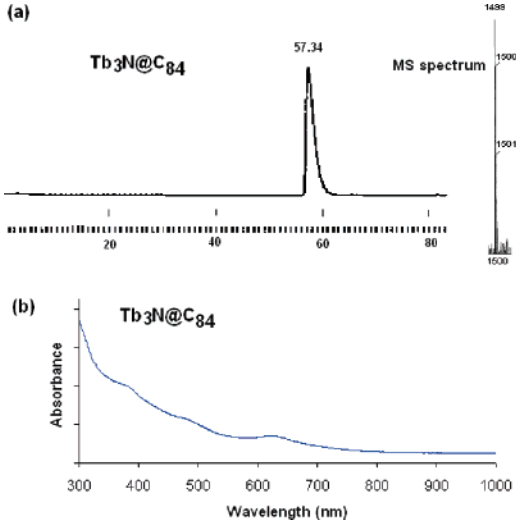

Figure 1. (a) The HPLC chromatogram and negative ion DCI MS spectrum of the pure isomer 2 of $Tb_3N@C_{84}$. 5PYE column (10 mm by 250 mm); 2.0 mL of toluene/min; 390 nm detection. (b) UV/vis of the pure isomer 2 of $Tb_3N@C_{84}$ in toluene solution.

Black parallelepipeds of $Tb_3N@C_{84}\cdot Ni^{II}(OEP)\cdot 2(C_6H_6)$ were obtained by diffusion of a benzene solution of the endofullerene into a benzene solution of Ni^{II}(OEP) and were utilized in the crystal structure determination.[11] Figure 2 shows a drawing of the $Tb_3N@C_{84}$ molecule and its orientation relative to the Ni^{II}(OEP) molecule. The figure caption gives some interatomic distances and angles. Figure 3 shows another view of the endofullerene molecule. Neither the endofullerene nor the porphyrin has any crystallographically imposed symmetry. As usual, all eight ethyl groups of the porphyrin surround the fullerene. The endofullerene is positioned so that a rather flat section of its outer surface makes contact with the planar porphyrin.

The carbon cage in $Tb_3N@C_{84}$ does not obey the isolated pentagon rule. There is one fused pentagon pair with C78 and C82 forming the critical junction. For a C_{84} cage, Nature can choose from the 24 isomers that conform to the IPR or it can select one of the 51 568 isomeric structures that do not conform to the IPR. The isomer found in this sample is the non-IPR isomer No. 51365 with C_s symmetry and the ring spiral code: 1 2 11 13 16 18 29 31 33 35 37 44.[1] Nevertheless, with so many isomeric structures to choose from, it is surprising to find that only two isomers of $Tb_3N@C_{84}$ are formed in significant amounts.

There is some disorder in the structure. While Tb1 has full occupancy, the sites designated as Tb2 and Tb3 have only 0.512(3) occupancy. There are additional Tb sites that come in pairs and combine with Tb1 to define three additional Tb_3N units. Sites

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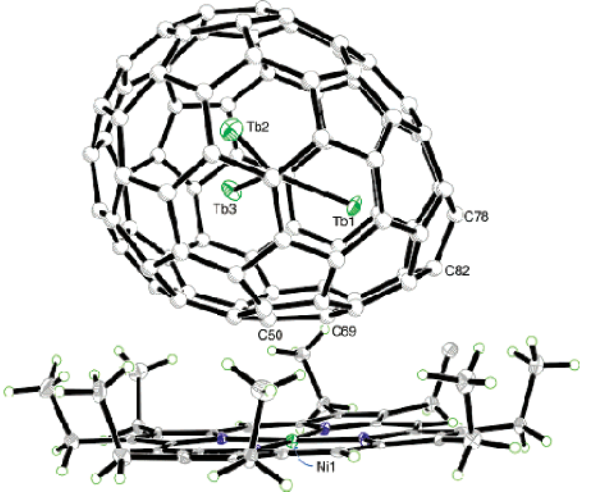

Figure 2. A view of the interaction of isomer 2 of $Tb_3N@C_{84}$ and Ni^{II}-(OEP) in $Tb_3N@C_{84}\cdot Ni^{II}(OEP)\cdot 2(C_6H_6)$ with uniform arbitrarily sized circles for the cage carbon atoms and 50% thermal ellipsoids for other atoms. Selected distances (Å) and angles (deg): Tb1−N1, 2.182(4); Tb2−N1, 2.130(4); Tb3−N1 2.120(4); Tb1−N1−Tb2, 124.5(2); Tb1−N1−Tb3, 114.60(18); Tb2−N1−Tb3, 120.70(19).

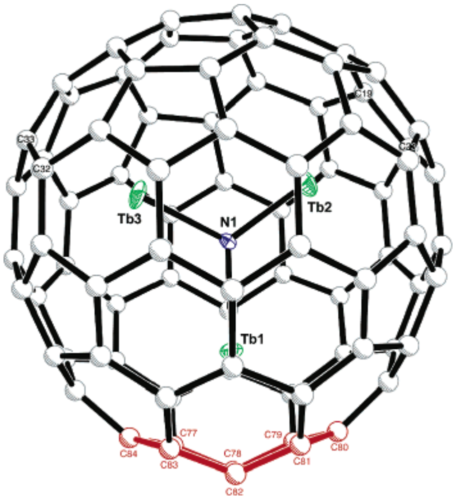

Figure 3. A view of isomer 2 of $Tb_3N@C_{84}$ with uniform arbitrarily sized circles for the carbon atoms and 50% thermal ellipsoids for other atoms. The pentalene portion is highlighted in red. The noncrystallographic mirror plane lies nearly parallel to the page.

Tb4 and Tb5 have 0.212(2) occupancy, while Tb6 and Tb7 have 0.229(3) occupancy. Finally, sites Tb8 and Tb9 have only 0.047(2) occupancy. Only the major site involving Tb1, Tb2, and Tb3 is shown in the figures.

The Tb_3N unit is planar in the major site as well as in all three minor sites. For the major site, the sum of the three Tb−N−Tb angles is 359.8°. The carbon cage also displays some disorder. 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.

Tb1 is situated within the fold of the pentalene unit formed by the fused pentagon pair. Within that unit, the Tb−C distances are shortest at the fold (Tb1−C82, 2.483(6); Tb1−C78, 2.502(6) Å) and longer for the four adjacent carbon atoms (Tb1−C83, 2.517(6); Tb1−C79, 2.523(6); Tb1−C81, 2.526(6); Tb1−C77, 2.527(6) Å). The positioning of Tb1 near the fused pentagon pair is similar to that of the scandium atoms within the three pentalene units of D_3 symmetric $Sc_3N@C_{68}$.[6b] It appears that a significant interaction between the metal and the fused pentagon pair may be responsible for the full occupancy of the Tb1 site. Tb2 is situated over a 5:6 ring junction with the shortest contacts involving Tb2−C23, 2.406(6), and Tb2−C19, 2.423(12) Å, while Tb3 is located near a 6:6 ring junction with close contacts of Tb3−C32, 2.333(6), and Tb3−C33, 2.385(6) Å.

Improved preparative and separation procedures are making many new endofullerenes with as yet unknown structures available in sufficient quantity to explore their physical properties and utilities.[10,12] The observation of a non-IPR structure for isomer 2 of $Tb_3N@C_{84}$ suggests that structural assignments for other endofullerenes need to consider non-IPR cages as well as the usual IPR isomers.[13]

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Supporting Information Available: Preparative and separation information for isomer 2 of $Tb_3N@C_{84}$. Drawings showing the disorder in the positions of the Tb_3N unit in isomer 2 of $Tb_3N@C_{84}$ and in part of the carbon cage. X-ray crystallographic data for $Tb_3N@C_{84}\cdot Ni^{II}(OEP)\cdot 2(C_6H_6)$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data for $C_{84}NTb_3\cdot C_{36}H_{44}N_4Ni\cdot 2(C_6H_6)$: black parallelepiped, triclinic, space group $P\bar{1}$, $a = 14.5782(13)$ Å, $b = 15.0328(14)$ Å, $c = 19.725(2)$ Å, $\alpha = 85.231(2)°$, $\beta = 89.668(2)°$, $\gamma = 62.199(2)°$, $V = 3807.9(6)$ Å^3, $Z = 2$, $D_c = 1.960$ Mg/m^3, $T = 90(2)$ K; $R1 = 0.091$, $wR2 = 0.0976$ for all data; conventional $R1 = 0.0470$ computed for 10 509 observed data ($I > 2\sigma(I)$) with 1 restraint and 968 parameters.
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