Endohedral metal carbides suggest an intriguing relationship to the growth mechanism of endohedral fullerenes; however, due to crystal quality requirements, only a half dozen of these have been characterized by single crystal X-ray diffraction. Likewise, few examples of non-isolated pentagon rule (non-IPR) endohedral fullerenes have been crystallographically characterized, beginning with Sc$_3$N@C$_{68}$ in 2003 [1]. Since that time, the use of synchrotron radiation has increased our ability to determine the structures of these relatively rare fullerenes. The metal clusters encaged in non-IPR fullerenes include Tb$_3$N, Gd$_3$N, Sc$_2$S and involve a range of cage sizes from C$_{66}$ to C$_{92}$. To date, the carbides include only C$_2$ fragments, cage sizes in the range C$_{68}$ to C$_{92}$ and the metals Sc, Ti, Y, and Gd. We recently determined the first crystal structure of a non-IPR endohedral that contains a metal carbide. That endohedral fullerene, paramagnetic Gd$_2$C$_2$@C$_{84}$, belongs to one of 51592 possible isomers of the C$_{84}$ cage, of which 24 follow the isolated pentagon rule (IPR). Our study reveals a single violation of the IPR; that is, the fullerene cage possesses one pentalene unit where two pentagons are touching. Theoretical calculations as well as $^{13}$C NMR studies anticipated this result for the diamagnetic Y$_2$C$_2@C_{84}$ congener. Geometric features, including positioning of the Gd$_2$C$_2$ unit within the cage in comparison to related carbide endohedrals will be presented.

1. INTRODUCTION

Fullerenes are a fascinating new form of elemental carbon whose discovery as cage-like molecules can be traced back to as recent as 1985. Since that time our curiosity about their formation, shapes and sizes, reactivity, and possible applications has driven an increasing number studies and of publications. Except for the most common empty cages of C$_{60}$ and C$_{70}$, so little of the less common fullerenes is synthesized at a time that characterization of fullerenes still presents an enormous challenge. Not the least of these challenges is their full 3-dimensional characterization, which can only be reliably achieved by single-crystal X-ray diffraction. Our laboratory has been fortunate to have access to two California synchrotrons, first the Stanford Synchrotron Radiation Laboratory and, more recently, the single crystal beam line 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. With the use of synchrotron
radiation, there are few limitations on crystal size, and high-resolution data are more accessible than with common laboratory sources. The high flux of the synchrotron enables us to select among the paucity of crystals for the most suitable specimen. Furthermore, the high-resolution data allow for better modeling of disorder and twinning, common features of these spherical molecules and their structures.

Among the known fullerenes, those with empty cages obey what is known as the isolated pentagon rule (IPR), a “rule” first described by Kroto [2] in recognition of the observation that all of the exactly twelve pentagons in the fullerene cage are surrounded by hexagons. Endohedral fullerenes are a special class of fullerenes that encapsulate other atoms. The C$_{60}$ fullerene has an inside diameter of 7 Å; He, Ne, Kr, Ar, Xe, H$_2$, N, P, and H$_2$O have been detected inside. Larger cages typically encapsulate metallic species that have strong interactions with the inside of the cage. Some representative contents are M, M$_2$, M$_3$N, Sc$_4$O$_2$, Sc$_4$O$_3$, Sc$_2$O, Sc$_2$S, Sc$_3$C$_2$, Sc$_2$C$_3$, Gd$_2$C$_2$. In certain endohedral fullerenes, the IPR is not obeyed and the carbon cage displays one, two or three locations where two pentagons are fused (called a pentalene fragment). A simple description of the basic geometry of any fullerene cage is based on the spiral algorithm. This principle was originally described by Manolopoulos, May and Down [3]. In order to describe the positions of the pentalene fragments, as well as those of all twelve pentagons present, a standard pentagon starting point is selected and then successive hexagons or pentagons are added in a spiral fashion until the cage is closed. If each hexagon and pentagon is numbered in sequence, the pattern can be simply represented by the numerical order of the twelve pentagons alone.

Not only are endohedral fullerenes distinctly different from empty cage fullerenes in their ability to violate the IPR, the metals and clusters that are encapsulated are known to transfer their charge such that the cage acquires a negative charge. In contrast, empty cages are considered to be neutral. Encapsulated group 2 elements such as Ca are divalent, group 3 elements such as Sc and Y are trivalent and group 4 elements are tetravalent. Lanthanide elements are considered to be +3 ions with a few exceptions (Sm, Yb, Eu and Tm are expected to be +2). Trimetallic nitride clusters, M$_3$N, nearly all +3 M ions, have a net charge of +6. A carbide such as Gd$_2$C$_2$ is +4. The number of electrons transferred to the cage dramatically changes the favored cage isomer. As IPR examples, Ce$_2$@I$_h$(7)-C$_{80}$ [4] and Tb$_3$N@I$_h$(7)-C$_{80}$ [5] represent cases where six electrons are transferred, while in Sc$_2$C$_2$@C$_{2v}$(5)-C$_{80}$ [6], four electrons are transferred, and in Yb@C$_{2v}$(3)-C$_{80}$ [7], two electrons are transferred. When the potential for non-IPR cages to occur is factored in, the number of cage isomer possibilities is exponentially greater.

The case of the C$_{84}$ endohedrals is illustrative. In 2006 we reported the first structure of a non-IPR cage of C$_{84}$ in the compound Tb$_3$N@C$_{84}$ with a single instance of fused pentagons [8]. There are 24 isomers that conform to the IPR for C$_{84}$, but 51568 that do not. The compound formed a cocystal with Ni$^{II}$(OEP) and two benzenes. The cage itself has mirror symmetry, and the isomer, written according to the spiral algorithm, is 51365: Tb$_3$N@C$_{84}$(51365)C$_{84}$•Ni$^{II}$(OEP)•2C$_6$H$_6$. Subsequently, the isostructural compounds involving Tm and Gd [9], and Y [10] were reported. Figure 1 shows the Gd fullerene together with the nearest molecule of Ni$^{II}$(OEP). Figure 2 shows the local geometry of the Gd$_3$N moiety.
The current status of the field of endohedral fullerenes has been recently reviewed [11]. Another review of the endohedrals focuses on the carbide cluster metallofullerene category [12]. The main subject of this report is the particularly challenging structure of the paramagnetic endohedral fullerene, Gd$_2$C$_2$@C$_{84}$. This molecule contains a fullerene cage with no point symmetry that is one of 51592 possible isomers and does not obey the IPR. Its synthesis was carried out by the Dorn group at Virginia Polytechnic Institute and State University, and the crystallography was carried out by the Balch/Olmstead group at UC Davis group with data obtained at the ALS. Remarkably, in 2012 Nagase and coworkers predicted the same cage structure for the diamagnetic compound in which Y replaces Gd, based upon extensive computations [13]. The synthesis and isolation of Y$_2$C$_2$@C$_{84}$ was reported by Dorn in 2012 [14] and its structure was expected to be non-IPR based on HPLC retention times and $^{13}$C NMR evidence. A publication that describes many aspects of this study of Gd$_2$C$_2$@C$_{84}$ and its possible role in fullerene cage formation is in press [15]. Here, we wish to expand on the structural aspects as elaborated by the team at the University of California, Davis.
2. EXPERIMENTAL

Preparation of Gd$_2$C$_2@C_1$(51383)-C$_{84}$. The compound was obtained by the electric arc method by vaporization of graphite rods packed with Gd$_2$O$_3$, graphite powder and metallic Cu. It was isolated from the soot together with several empty cage and endohedral fullerenes following the previously reported procedure [16].

Crystal Structure Analysis of Gd$_2$C$_2@C_1$(51383)-C$_{84}$•Ni$^{II}$(OEP)•1.75(toluene)•0.25(benzene). Black parallelepipeds were obtained by diffusion of a toluene solution of the endohedral into a benzene solution of nickel octaethylporphyrin. The crystal selected for data collection was a black plate of dimensions 0.05 x 0.15 x 0.27 mm. It was mounted in the 90 K nitrogen cold stream provided by an Oxford Cryostream low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with an ApexII CCD detector. Data were collected with the use of synchrotron radiation ($\lambda = 0.77490$ Å) at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley Laboratory. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on $F^2$ (SHEXL-2012) [17]. The crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC 928943).

The initial solution revealed a molecule of Ni$^{II}$(OEP), disordered sites of toluene/benzene and three Gd positions. One orientation for a C$_{84}$ cage, and disordered encapsulated Gd$_2$C$_2$, were found by repeated cycles of least-squares refinement and difference Fourier maps. At least one more orientation was clearly present. Since the cage was found to have $C_1$ symmetry, a second orientation of opposite hand was eventually placed by successive difference maps and refinement of inverted C$_1$(51383)-C$_{84}$ rigid groups. Each enantiomer was assigned 0.5 occupancy. In the final cycles of refinement, in order to reduce correlation effects and achieve convergence, the carbons of the ball were freely refined but kept isotropic. A SIMU 0.008 command was applied to smooth the displacement parameters. Some carbons were refined with equal isotropic thermal parameters due to similar positions and high correlations. In addition, a loose distance restraint of 1.429(15) Å was applied to C-C all distances except for the C-C bond of the adjacent pentagons, which was restrained to 1.410(15) Å. The structure also shows disorder in the Gd sites. The final model included eighteen Gd positions. Gd1 and Gd10 are the predominant sites on opposite sides of the C$_2$ group, with occupancies of 0.52 and 0.34, respectively. Gd2 – Gd9 have occupancies of 0.11, 0.11, 0.08, 0.05, 0.04, 0.03, 0.03, 0.03, while Gd11 – Gd18 have occupancies of 0.25, 0.20, 0.06, 0.05, 0.02, 0.03, 0.03, 0.02, respectively. The total occupancy for all Gd positions in the asymmetric unit is 2.0. Initial site occupancies were refined, and they were fixed in the final cycles of refinement. All except Gd16, Gd17, and Gd18 were allowed to become anisotropic. There is also some disorder in the carbide: C85 and C86 are the major positions at 0.75 fractional occupancy each; C86B is an alternative position at 0.50 occupancy. The total occupancy for these carbide positions is 2.0. There are two solvate sites. One is occupied by overlapping toluene molecules at equal occupancy while the other contains 0.75 toluene and 0.25 benzene molecules. These molecules were refined as rigid groups with idealized geometry. The numbering scheme was chosen to match that of the computed structure of Y$_2$C$_2@C_1$(51383)-C$_{84}$ [5]. Crystal data: C$_{86}$Gd$_2$•C$_{36}$H$_{44}$N$_4$Ni•1.75(C$_7$H$_8$)•0.25(C$_6$H$_6$), $M_w$ = 2119.58, monoclinic, $P2_1/c$, $a = 20.4825(7)$ Å, $b = 14.8334(5)$ Å, $c = 25.3877$ Å, $\beta = 96.261(2)^\circ$, $V = 7667.4(5)$ Å$^3$, $Z = 4$, $R_1$ [18147 reflections with $I > 2\sigma(I)] = 0.115$, $wR^2$ (all 29336 data) = 0.329, 1353 parameters, 511 restraints.
3. RESULTS
The asymmetric unit contains sites of one endohedral fullerene, one porphyrin, and two solvate molecules. There is no crystallographic symmetry. As depicted Figure 3, the octaethyl groups of \( \text{Ni}^{II}(\text{OEP}) \) host the fullerene. In the figure, disorder is removed for clarity and only one enantiomer is shown. A notable part of the cage is the occurrence of one pentalene site; thus a non-IPR cage is present. The solvate sites are orientationally disordered and one is shared between toluene and benzene. The back-to-back porphyrin arrangement brings the inversion-related \( \text{Ni}1 \ldots \text{Ni}1' \) contact to 3.477(2) Å.

![Figure 3](image1.png)

**Figure 3.** \( \text{Gd}_2\text{C}_2@\text{C}_{1}(51383)-\text{C}_{84}^*\text{Ni}^{II}(\text{OEP}) \) with two toluene sites and inversion-related \( \text{Ni}^{II}(\text{OEP}) \).

Figure 4 is an idealized view of two different enantiomers of the \( \text{C}_{1}(51383)-\text{C}_{84} \) cage. However, in the crystal structure, the two “noses” do not point in opposite directions, but rather are considerably overlapped, rotated by only 12° with respect to the center of their cages.

![Figure 4](image2.png)

**Figure 4.** The two enantiomers of \( \text{Gd}_2\text{C}_2@\text{C}_{1}(51383)-\text{C}_{84} \) depicted as mirror images.

We have confirmed that the fullerene site contains a racemic mixture of the non-IPR \( \text{C}_1 \) isomer 51383 with ring spiral 1 2 11 13 16 19 28 31 33 35 37 44. During solution of the structure, one enantiomer was assembled by tedious atom picking. The opposite enantiomer then appeared in essentially its entirety in a difference Fourier map. We believe that the availability of synchrotron data was the key to our successful solution of this structure.
In Figure 5 we show the orientation of one of the two enantiomers in relation to the host molecule Ni\textsuperscript{II}(OEP) which offers an interesting comparison to the related trimetallic nitride structure shown in Figure 1.

Figure 5. A view of Gd\textsubscript{2}C\textsubscript{2}@C\textsubscript{1}(51383)-C\textsubscript{84}*Ni\textsuperscript{II}(OEP) for one of the two enantiomers.

Figure 6. The position of the Gd\textsubscript{2}C\textsubscript{2} unit inside the C1-C84 fullerene cage for one of the two enantiomers.

Figure 6 shows the major Gd and carbide sites in one of the C1-C84 cages. The C1B-C84B (“B” refers to the second enantiomer) cage looks similar. Although there is considerable disorder in the Gd positions, the major location (Gd1, 54% occupancy) is close to the unique pentalene region where two pentagons are fused to give a nose-like effect to the cage. The other prominent location is approximately \(\eta^6\) to a hexagonal ring. The closest Gd−C contacts between Gd1 and Gd10 in C1-C84 are shown. Similar contacts in C1B-C84B occur using Gd1 and Gd11. The two closest distances between Gd1 and the cage are 2.300(19) and 2.383(14) Å. The six closest distances between Gd10 and the cage are in the range 2.376(18)-2.63(2) with an average of 2.49 Å. The Gd\textsubscript{2}C\textsubscript{2} unit is asymmetrically placed along this span of the C\textsubscript{84} cage. Distances between Gd1 and the carbide are longer than those between Gd10 and the carbide. For Gd1 these distances are 2.541(9) and 2.487(10) Å, while for Gd10 they are 2.314(9) and 2.332(10) Å. In the major site shown, C85-C86, the carbide C-C distance is 1.230(14) Å; in the minor site, C85-C86B, it is 1.327(19) Å. Consideration of the “butterfly” shape of Gd1-C85-C86-Gd10 yields a dihedral angle between the two GdC\textsubscript{2} planes of 122.7° and the enantiomeric cage consisting of Gd1-C85-C86B-Gd11 yields a corresponding angle of 123.6°. Clearly, as shown in Figure 7, disorder in the Gd positions creates a large range of dihedral angles, and the angle cannot be specifically assigned for the minor locations.
DISCUSSION

The Stone-Wales transformation and the relationship between $M_3N@C_{84}$ and $M_2C_2@C_{84}$ cages. Since we have found that both the non-IPR $M_3N@C_{84}$ and $M_2C_2@C_{84}$ cages possess one instance of a fused pentagon, yet they differ in overall point symmetries and also in the number of electrons transferred to the cage, we sought a simple relationship between them. The answer is often found to be one or more Stone-Wales transformations of the type depicted in Figure 8, which exchanges two pentagons and two hexagons via a rotation by 90° of a central C-C bond \[18\]. In fact, the difference between the two cages can be described by one such transformation, as is shown by the red-colored carbons in the figure. It also apparent from Figure 8 that the “lumpiness” of the two cages is different--a consequence of different cage isomers, and of the geometric constraints of the cage contents.

Figure 8. Stone-Wales relationship between the carbon cages of $Gd_3N@C_8(51365)-C_{84}$ (A) and $Gd_2C_2@C_1(51383)-C_{84}$ (B). Pentalene carbons are shown in green and the key atoms that represent the one Stone-Wales transformation that interconverts these cage isomers are shown in red.
Computational analyses of endohedral carbides

The computational results that have been reported in the literature concern acetylenic carbides of the type Sc\textsubscript{2}C\textsubscript{2}, Ti\textsubscript{2}C\textsubscript{2}, Y\textsubscript{2}C\textsubscript{2}, Gd\textsubscript{2}C\textsubscript{2}, Lu\textsubscript{2}C\textsubscript{2}. Based on a simple electrostatic model in which the C\textsubscript{2} unit bears a 2- charge and the metal is 3+, a symmetrical planar structure might be expected, as seen in some organometallic examples [21]. However, encapsulation by a fullerene cage may not allow this arrangement due to the constraints of cage size, adduct formation, and other localized charge distributions. Thus, computations [11, 14, 19, 20] have predicted a range of geometries, as depicted in Figure 9. In the ionic model for endohedral fullerenes, the M\textsubscript{2}C\textsubscript{2} unit is a 4+ cation and transfers 4 electrons to the cage.

Figure 9. In the absence of encapsulation, the top left arrangement of the M\textsubscript{2}C\textsubscript{2} unit is favorable, but, inside a fullerene, arrangements as shown on the right have been observed.

Crystallographic descriptions of the M\textsubscript{2}C\textsubscript{2} unit

The \(\sigma\)-type linear arrangements shown at the left hand side of Figure 9 have not been crystallographically observed inside fullerenes. Commonly, both orientational disorder in the cage and internal positional disorder occur, as is the case in the structure of Gd\textsubscript{2}C\textsubscript{2}@C\textsubscript{1}(51383)-C\textsubscript{84} reported here, and therefore, rather high uncertainty is associated with the geometry of the M\textsubscript{2}C\textsubscript{2} unit. Our understanding of the geometry is derived from the atom positions with the highest occupancies. The unusual asymmetry in the {cage}...Gd...[C2]...Gd...{cage} placement was not predicted by computation on the Y congener [13]. We note, however, that a strong attraction of the pentalene for the M\textsuperscript{3+} ion was observed in other structures, for example in the IPR C\textsubscript{84} trimetallic nitride endohedrals [8, 9]. Certain trends are seen. For example, as shown in Table 1, the larger metal-metal distances can be correlated with wider dihedral angles. A cage
that is large enough to accommodate a 180° dihedral angle has not yet been reported. The largest known carbide cluster endohedral is Gd$_2$C$_2@D_3$-C$_{92}$ [22]. The longest dimension of the $D_3$-C$_{92}$ cage is 9.43 Å, and the dihedral angle range of 154-161° is in accord with typical required distances between the metal and the carbons of the cage. As the cage contracts to ca. 8.2 Å in Gd$_2$C$_2@C_1$-C$_{84}$, repulsions between the metal and carbons require compression of the M$_2$C$_2$ unit, and the more acute angles in the range of 123-124° are observed. One of the enduring fascinations of the endohedral carbide structures is the observation of the close interplay between steric effects and bending strain of the cluster. As more structural details become available, computational results will aid in understanding the complementary roles played by electrostatic effects and covalent bonding.

TABLE 1

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