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Does Gd@C_{82} Have an Anomalous Endohedral Structure? Synthesis and Single Crystal X-ray Structure of the Carbene Adduct

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Endohedral metallofullerenes have attracted considerable interest as promising spherical molecules for material and biomedical applications, because of their unique properties that are unexpected from empty fullerenes.[1] It is the focus of interest to determine cage structures and metal positions, because these are essential for the properties and reactivities of endohedral metallofullerenes. Since the first extraction of La@C_{82} in 1991,[2] M@C_{82} (M = group 3 metals and lanthanides) has been known as a representative monometallofullerene. Theoretical calculations have predicted that the M atom is mostly encapsulated inside the C_{2v} cage of C_{82}.[3,4] This prediction has been verified for metals such as M = Y,[5] La,[6−8] Ce,[9] and Pr[10] by measuring the ^{13}C NMR spectra of the diamagnetic anion of M@C_{82} or from the X-ray crystal analysis of the La@C_{82} carbene adduct.[7] The C_{2v} cage structures of Sc@C_{82}[11] and La@C_{82}[12] have been also found by the MEM (maximum entropy method)/Rietveld analysis of synchrotron X-ray powder diffraction data. In addition, the MEM/Rietveld analysis has shown that the Sc and La atoms are located at an off-centered position near a hexagonal ring of the C_{2v}-C_{82} cage. This agrees with theoretical prediction.[4] The X-ray single crystal analysis and theoretical calculations of La@C_{82}(Ad) (Ad = adamantylidene) have revealed that the La position is little changed by the Ad addition.[7] The paramagnetic NMR spectral analysis and theoretical calculations of Ce@C_{82} and its anion have shown that the Ce atom even in the Ce@C_{82} anion is also located at an off-centered position adjacent to a hexagonal ring along the C_2 axis of the C_{2v}-C_{82} cage.[13]

From the MEM/Rietveld analysis, however, it has been recently claimed that Gd@C_{82}[14] and Eu@C_{82}[15] have an exceptional anomalous endohedral structure, in which the metal atom having f electrons is located near the C−C double bond on the opposite side of the C_{2v}-C_{82} cage along the C_2 axis. This claim disagrees with theoretical calculations[4,16−18] and experimental studies.[19,20] According to the recent theoretical calculations of Gd@C_{82} and Eu@C_{82}, the anomalous structures found from the MEM/Rietveld analysis are highly unstable and do not correspond to energy minima.[17] In this context, we have carried out the single crystal X-ray crystallographic analysis of the Gd@C_{82} carbene adduct (Gd@C_{82}(Ad)(1)) together with theoretical calculations. These results do not support the anomalous structure of Gd@C_{82}.

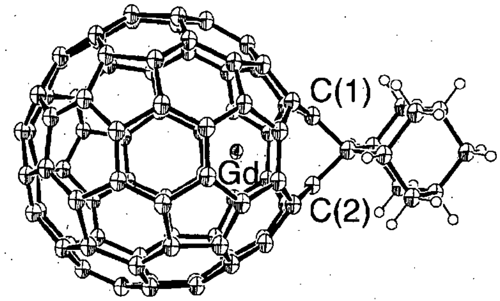
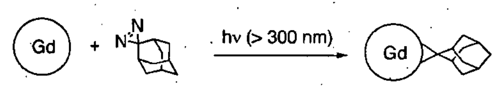


Figure 1. ORTEP drawing of one enantiomeric isomer of Gd@C_{82}(Ad) (1) showing thermal ellipsoids at the 50% probability level. The CS_2 and 1,2,4-trichlorobenzene molecules are omitted for clarity.

Irradiation of a toluene solution of Gd@C_{82}[21] (2 mg, 7.8×10^{-5} M) and an excess molar amount of 2-adamantane-2,3-[3*H*]-diazirine (**2**) in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 300 nm) resulted in the formation of the adduct, Gd@C_{82}(Ad) (**1**) in a 95% yield, which was purified by preparative HPLC (eq 1). LD-TOF mass spectrometry of **1** ($C_{92}H_{14}$Gd, mass *m/z* 1410) exhibits a molecular ion peak at *m/z* 1410−1407 and a peak at *m/z* 1276−1273 (Gd@C_{82}) due to the loss of the Ad group. The UV−visible-near-infrared absorption spectrum of **1** is similar to that of the pristine Gd@C_{82}. These results suggest that **1** retains the essential electronic and structural character of Gd@C_{82}.



Gd@C_{82} **2** **1** (1)

The structure of **1** determined by the X-ray crystal analysis[22] is shown in Figure 1. The structural aspects are very similar to those for La@C_{82}(Ad). As is apparent from Figure 1, the fullerene cage of **1** originates from the C_{2v} isomer of C_{82} and the Gd atom is located at a single site. It is notable that the Gd atom is located at an off-centered position near a hexagonal ring in the C_{2v}-C_{82} cage, as found for M@C_{82} (M = Sc[11] and La[12]) and La@C_{82}(Ad).[7] The C(1)−C(2) distance is 2.100 Å, indicative of an open structure. The Gd−C(1) and Gd−C(2) distances are 2.515 and 2.523 Å, respectively. The X-ray data collected at 90, 213, and 293 K reveal

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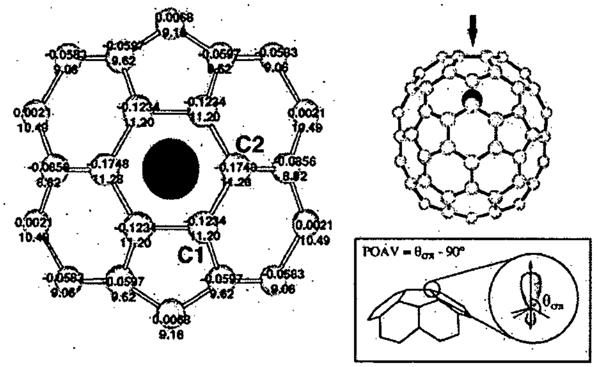

Figure 2. Selected charge densities (upper) and POAV ($\theta_{\sigma\pi} - 90°$) values (lower) in Gd@C_{82}.

that the Gd atom remains at the same position regardless of temperatures, as shown in Figure 1.

Since there are 24 nonequivalent carbons and 19 nonequivalent 6−6 bonds in Gd@C_{82}, the addition of Ad may occur at several sites to afford several monoadduct isomers. Although the reactions of Gd@C_{82} with organic reagents[23] have been reported so far, no structural determination of the adducts has been reported yet.

The selective formation of **1** (the structure in Figure 1) can be explained using the reaction of the photochemically generated Ad with Gd@C_{82}, as in the La@C_{82} case.[7] The local strain on cage carbons plays an important role in determining the reactivity. The pyramidalization angles from the π-orbital axis vector analysis POAV ($\theta_{\sigma\pi} - 90°$) values provide a useful index of the local strain.[24] The Mulliken charge densities and POAV ($\theta_{\sigma\pi} - 90°$) values calculated for Gd@C_{82} are shown in Figure 2.[25] Both values are found to be large for the carbons in the six-membered ring nearest to the Gd atom. This suggests that the electrophilic Ad selectively attacks the highly electron-rich and strained carbons in the six-membered ring.[26] In fact, the addition of Ad takes place on the carbon atoms, C(1) and C(2) (Figure 2), as indicated by the X-ray crystal structure (Figure 1). The structural confirmation of Gd@C_{82} by X-ray single crystal structure analysis is in progress and will be reported in due course.

The single crystal X-ray crystallographic analysis of Gd@C_{82}(Ad) (**1**) suggests that Gd@C_{82} has a normal endohedral structure in which the Gd atom is located at an off-centered position near a hexagonal ring (not near the C−C double bond) along the C_2 axis of the C_{2v}-C_{82} cage, as does M@C_{82} (M = Sc[11] and La[12]). This indicates that the MEM/Rietveld analysis is not always reliable for metal positions[17,27] as well as cage structures,[28,29] though it has been widely used for structural determination of endohedral metallofullerenes.[30] The highly selective derivatization of Gd@C_{82} suggests that an encapsulated metal plays an important role in controlling the reactivity and selectivity of fullerenes. Synthesis of target molecules with a high selectivity and reactivity is important for accurate organic synthesis, especially for endohedral metallofullerenes whose preparation and isolation are difficult in large-scale quantities.

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Supporting Information Available: Complete refs 6 and 7; analytical HPLC profile and cyclic and differential pulse voltammogram of **1**; details of theoretical calculation and the X-ray crystallographic data collection and structure refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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