Analysis of Lanthanide-Induced NMR Shifts of the Ce@C$_{82}$ Anion

Michio Yamada,[†] Takatsugu Wakahara,[†] Yongfu Lian,[†] Takahiro Tsuchiya,[†] Takeshi Akasaka,*,[†]
Markus Waelchli,[‡] Naomi Mizorogi,[§] Shigeru Nagase,*,[§] and Karl M. Kadish[¶]

*Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan,
Bruker Biospin K. K., Tsukuba, Ibaraki 305-0051, Japan, Department of Theoretical Molecular Science, Institute
for Molecular Science, Okazaki, Aichi 444-8585, Japan, and University of Houston, Houston, Texas 77204-5003*

Received August 26, 2005; E-mail: akasaka@tara.tsukuba.ac.jp; nagase@ims.ac.jp

Endohedral metallofullerenes[1] have attracted wide interest because of their possible applications in the fields of nanomaterial and biomedical science. La@C$_{82}$ has been recognized as a prototype of endohedral metallofullerenes since its first extraction in 1991 by Smalley and co-workers.[2] Meanwhile, much attention has been paid to encapsulation of lanthanide atoms having f electrons, as seen for Tm@C$_{82}$,[3] Ce@C$_{82}$,[4] Pr@C$_{82}$,[5] Gd@C$_{82}$,[6] and Eu@C$_{82}$.[7] For their electronic and magnetic properties, cage structures and metal positions play an important role.[1] Recently, we have succeeded in determining the cage frameworks of La@C$_{82}$,[8] Ce@C$_{82}$,[9] Pr@C$_{82}$,[10] and Y@C$_{82}$[11] by measuring the ^{13}C NMR spectra of their anions. All these carbon cages originate from the C$_{2v}$ isomer of C$_{82}$. From the MEM (maximum entropy method)/Rietveld analysis of synchrotron powder diffraction data of Sc@C$_{82}$,[12] Y@C$_{82}$,[13] and La@C$_{82}$,[14] Takata, Shinohara, and co-workers have determined that the metal atom is located at an off-centered position on the C$_2$ axis adjacent to a hexagonal ring of the C$_{82}$ cage. These results agree with theoretical prediction.[15] From the MEM/Rietveld analysis, however, it was recently reported that Eu@C$_{82}$[7] and Gd@C$_{82}$[16] have an anomalous structure, in which the metal atom having f electrons is located on the C$_2$ axis but is adjacent to the C−C double bond on the opposite side of the C$_{2v}$−C$_{82}$ cage. We report here the positional determination of the Ce (4f^{1}5d^{1}6s^2) atom in Ce@C$_{82}$ by means of paramagnetic NMR spectral analysis of the Ce@C$_{82}$ anion and density functional calculations.

First, we revealed the mapping of the bond connectivity in the carbon cage of [Ce@C$_{82}$]$^-$ and assigned the NMR lines by 2D INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) NMR measurements.[17] Figure 1 shows the 2D INADEQUATE NMR spectrum of [Ce@C$_{82}$]$^-$. Two-bonded carbon atoms share a double quantum frequency in the vertical dimension, and each peak appears at the two respective chemical shifts in the horizontal dimension. As shown in Figure 1, the chemical shifts of all carbon atoms in [Ce@C$_{82}$]$^-$ are completely assigned,[18] as was recently done for [La@C$_{82}$]$^-$.[19] This complete assignment makes it possible to analyze the following Ce-induced NMR shifts.

All carbon chemical shifts (δ) show considerable temperature dependence originating from the f electron spin remaining on Ce.[20] The chemical shifts of paramagnetic molecules in solutions are generally expressed as a sum of three contributions from diamagnetic (δ_{dia}), Fermi contact (δ_{fc}), and pseudocontact (δ_{pc}) shifts

$$\delta = \delta_{dia} + \delta_{fc} + \delta_{pc}$$

where the paramagnetic δ_{fc} and δ_{pc} are proportional to T^{-1} and

† University of Tsukuba.
‡ Bruker Biospin K. K.
§ Institute for Molecular Science.
¶ University of Houston.
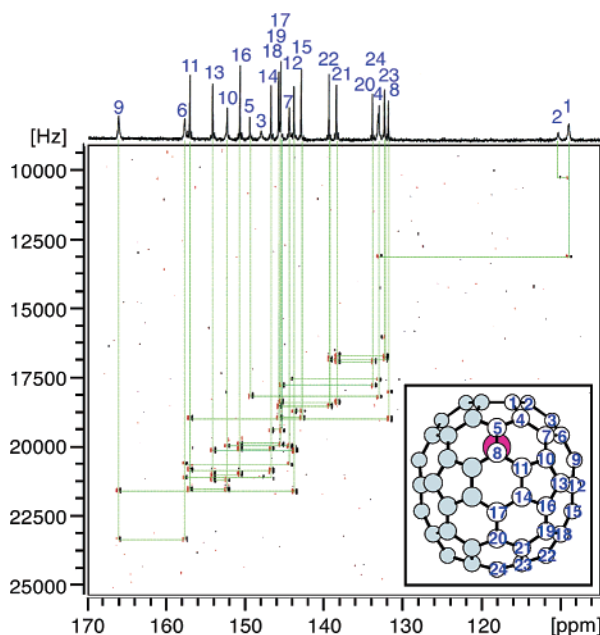
Figure 1. Two-dimensional INADEQUATE NMR spectrum of [Ce@C$_{82}$]$^-$ at 288 K; 125 MHz, in acetone-d_6/CS$_2$ (2/1). Inset shows the schematic structure of Ce@C$_{82}$.

T^{-2} (T = absolute temperature), respectively.[21] The δ_{dia} values correspond to the carbon chemical shifts of the diamagnetic [La@C$_{82}$]$^-$. As clearly shown in Figure S3, the values at $T^{-1} = 0$ extrapolated by the line-fitting plot with T^{-1}, which correspond to the δ_{dia} values of [Ce@C$_{82}$]$^-$, deviate significantly from the observed carbon chemical shifts of [La@C$_{82}$]$^-$.[8] On the other hand, the values at $T^{-2} = 0$ on the line-fitting plot with T^{-2} are in good agreement with the observed carbon chemical shifts of [La@C$_{82}$]$^-$, as shown in Figure S4. These suggest that δ_{pc} makes a much larger contribution than δ_{fc} for the chemical shifts of [Ce@C$_{82}$]$^-$, as is apparent from the fact that there is no significant connection between the Ce atom and cage carbons. As Figure 2 shows, the agreement in the chemical shift pattern between [Ce@C$_{82}$]$^-$ and [La@C$_{82}$]$^-$ also confirms a dominant pseudocontact mechanism. The δ_{pc} is briefly written in the following equation

$$\delta_{pc} = \frac{C(3\cos^2\theta - 1)}{r^3 T^2}$$

where r is the distance between Ce and cage carbons, θ is the angle between the r vector and the C$_2$ axis of Ce@C$_{82}$ (see Figure 3), and C is a common constant for all the cage carbons. To obtain the optimal distance (x) between Ce and the center of the hexagonal ring along the C$_2$ axis, full geometry optimization was carried out
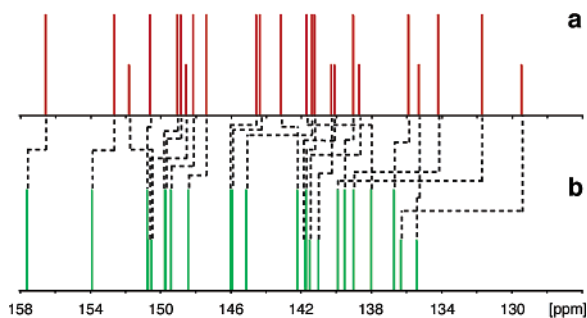
Figure 2. (a) Diamagnetic δ_{dia} pattern of $[Ce@C_{82}]^-$. (b) Observed ^{13}C NMR pattern of $[La@C_{82}]^-$.[8]
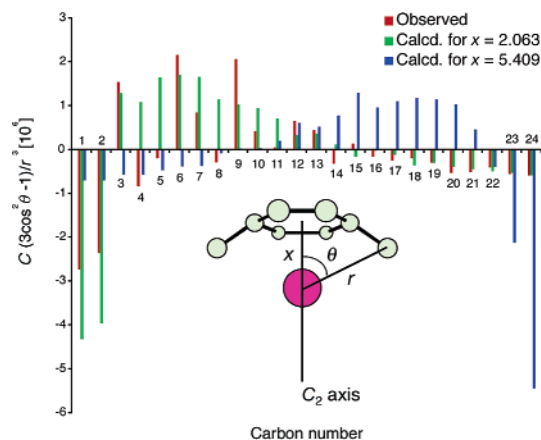
Figure 3. Calculated and observed values of $C(3\cos^2\theta - 1)/r^3$ for each carbon atom. The calculated value of $C(24)$ for $x = 2.063$ Å is normalized to the observed one by using $C = -6.827 \times 10^7$.

for $[Ce@C_{82}]^-$ using density functional theory.[22] The optimal x is 2.063 Å when the Ce atom is located near the hexagonal ring, while it is 5.409 Å when Ce is located near the C–C double bond on the opposite end. It is shown in Figure 3 how the δ_{pc} values change when the Ce atom moves along the C_2 axis from the position ($x = 2.063$ Å) near the hexagon to the position ($x = 5.409$ Å) near the C–C double bond. The δ_{pc} values obtained for $x = 2.063$ Å agree much better with the observed values than those for $x = 5.409$ Å. In addition, density functional calculations show that the optimized endohedral structure of $[Ce@C_{82}]^-$ with $x = 2.063$ Å is 42.4 kcal/mol more stable than the corresponding structure with $x = 5.409$ Å.[22,23] As is apparent from these results, the Ce atom in $[Ce@C_{82}]^-$ is located at an off-centered position adjacent to the hexagonal ring, unlike the Eu and Gd atoms in $Eu@C_{82}$ and $Gd@C_{82}$. As Figure 3 shows, the δ_{pc} values of the carbon atoms (C(1)–C(8)) near the Ce atom deviate from the observed values. These deviations may result from the point charge model for the Ce atom since the Ce atom oscillates around the energy minimum.

In conclusion, the Ce atom in $Ce@C_{82}$ as well as $[Ce@C_{82}]^-$ is located at an off-centered position adjacent to a hexagonal ring along the C_2 axis of the C_{2v}–C_{82} cage,[23] as has been found for $M@C_{82}$ (M = Sc, Y, and La). This is in sharp contrast with the Eu and Gd positions determined recently by the MEM/Rietveld method for $Eu@C_{82}$ and $Gd@C_{82}$.[24] It is expected that the paramagnetic NMR spectral analysis is a useful method to determine the metal position in paramagnetic endohedral metallofullerenes having f electrons.

Supporting Information Available: Complete refs 8, 9, 10, and 26, general procedure, expanded Figure 1, detail of the equations of Fermi contact and pseudocontact interactions, line-fitting plot (chemical shift vs T^{-1} and T^{-2}), the plots of the sum of the squares of the residuals against x, and the data tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA055882M