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Structural Study of Three Isomers of Tm@C_{82} by ^{13}C NMR Spectroscopy

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Received November 30, 2000. Revised Manuscript Received June 7, 2001

Abstract: The ^{13}C NMR spectra were measured for three isomers of Tm@C_{82}, which is one of the divalent metallofullerenes. The molecular symmetries were determined for each isomer: isomer I has C_s symmetry, isomer II has C_2 symmetry, and isomer III has C_{2v} symmetry. Moreover the cage structure of Tm@C_{82}(III) was found to be C_{82}(9). As a result, it was revealed that Tm@C_{82}(III) has a cage identical to that of La@C_{82}, which is one of the trivalent metallofullerenes.

Introduction

Lanthanoid-containing metallofullerenes with C_{82} cages, M@C_{82} (M is a lanthanoid metal atom), are the most widely investigated metallofullerenes. According to the oxidation state of the metal atom inside, they are classified into two groups; in one the metal atom takes the divalent state, and in the other it takes the trivalent state.[1] Many researchers have been interested in whether the two types of metallofullerenes have a common cage. Tm@C_{82} is one of the divalent metallofullerenes,[2−4] while La@C_{82} is one of the trivalent metallofullerenes.[5] Dunsch et al. measured the ^{13}C NMR spectra of three isomers of Tm@C_{82} and assigned their symmetries: C_s, C_{3v}, and C_s for isomer I, II, and III, respectively.[6] Recently, Akasaka et al. measured the ^{13}C NMR of La@C_{82} anion produced electrochemically and determined that La@C_{82} has C_{2v} symmetry.[7] According to their results, the two types of metallofullerenes possess no common cage. On the contrary, on the basis of the transmutation experiment of a metal atom, Sueki et al. suggested that isomer III of the divalent metallofullerenes has the same carbon cage as the trivalent metallofullerene.[8,9] This contradiction prevents us from gaining further understanding of metallofullerenes. In the present study, to resolve the contradiction, we also isolated the same three isomers of Tm@C_{82} as Dunsch et al. and measured their ^{13}C NMR spectra. Because Tm@C_{82} is a paramagnetic molecule, the range of ^{13}C NMR signals are too wide, making it difficult to find signals with typical spectral widths; thus, we imagined that Dunsch et al. did not find all the signals and failed to assign the symmetries correctly. In fact, the symmetries determined by us are C_s, C_2, and C_{2v} for isomer I, II, and III, respectively, which are different from those assigned by Dunsch et al. Our results have revealed that isomer III of Tm@C_{82} has the same cage as La@C_{82}.

Experimental Section

The soot containing Tm@C_{82} was produced by direct current (600 A) arc discharge of a Tm/C composite rod under a 180 Torr He atmosphere. Both the empty fullerenes and metallofullerenes were extracted from the soot by refluxing for 8 h with 1,2,4-trichlorobenzene. The isolation of three isomers of Tm@C_{82} was accomplished by four-stage high-performance liquid chromatography (HPLC). In all the stages, toluene was used as eluent, and the flow rate was 12 mL/min. At the first stage, a Buckyprep column (20 mm × 250 mm) was used for roughly separating three isomers of Tm@C_{82} from other fullerenes. Tm@C_{82} was found in the tail of a hollow C_{84} fraction. At the second stage, Tm@C_{82}(I) was separated from the other two isomers by using two Buckyprep columns (20 mm × 250 mm). At the third and fourth stages for Tm@C_{82}(I), two Buckyprep columns (20 mm × 250 mm) and a 5PBB column (20 mm × 250 mm) were employed for each; empty fullerenes were removed, and Tm@C_{82}(I) was isolated. At the third stage for Tm@C_{82}(II) and Tm@C_{82}(III), they were roughly separated from each other, and the empty fullerenes were removed by using two Buckyprep columns (20 mm × 250 mm). At the fourth stage, two isomers were completely separated from each other by using a Buckyclutcher column (20 mm × 250 mm).

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(6) The isomer names given by us are different from those given by Dunsch et al. The names I, II, and III in our work correspond to the names B, A, and C in their work, respectively. The correspondence was confirmed by comparing the absorption spectra of each isomer. In this report, the former nomenclature was utilized because it is useful to compare with other divalent metallofullerenes. Dunsch, L.; Kuran, P.; Kirbach, U.; Scheller, D. *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; The Electrochemical Society, Inc.: Pennington, 1997; Vol. 4, pp 523−536.

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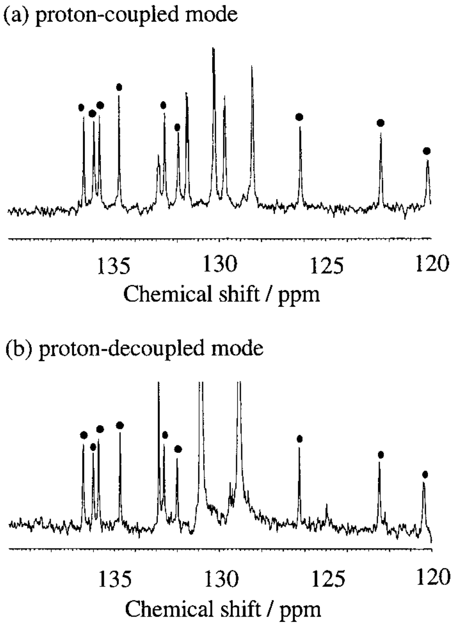

Figure 1. ^{13}C NMR spectra (125 MHz, CS$_2$) of Tm@C$_{82}$(II); (a) and (b) were measured at room temperature in a proton-coupled mode and a proton-decoupled mode, respectively. The intensity of each peak marked with a solid circle is not changed

The purity of isolated species was confirmed by LD-TOF-MS, and each isomer was identified with those reported by Dunsch et al. by comparing the absorption spectra. Relative yields of three isomers are the almost same, although we cannot determine the absolute yield quantitatively. The ^{13}C NMR spectra were measured at 125 MHz in CS$_2$ solvent with 5% 1,1,2,2-tetrachloroethane-d_2 as an internal lock. Each solution was almost saturated. The signals were accumulated for 3 or 4 days.

The Peak Assignment Methods of ^{13}C NMR Spectra

The method of peak assignment is explained for the case of Tm@C$_{82}$(II) as an example. Figure 1 shows a part (120−140 ppm) of the ^{13}C NMR spectra of Tm@C$_{82}$(II); (a) and (b) were measured in a proton-coupled mode and a proton-decoupled mode, respectively. In both spectra, the intensity of each peak marked with a solid circle is not changed, although the intensity of other peaks is changed. This means that the latter peaks come from the carbon atoms connected to a proton, that is, these carbons belong to impurities. Figure 2 shows a portion (110−140 ppm) of the temperature-dependent ^{13}C NMR spectra of Tm@C$_{82}$(II). The peaks marked with a solid circle show temperature-dependent shifts. On the other hand, other peaks have no such dependence. Tm@C$_{82}$ also shows ESR signals at very low temperature; thus, it is a paramagnetic molecule. In general, the NMR signals of a paramagnetic molecule show temperature-dependent shifts; therefore, the peaks that did not shift were assigned to impurities. The results obtained by the two different methods of peak assignment are completely consistent with each other, and we assigned the impurity to di-2-ethylhexyl phthalate.

Results

Parts a, b, and c of Figure 3 show the ^{13}C NMR spectra of three isomers of Tm@C$_{82}$, respectively; the peaks assigned to Tm@C$_{82}$ are marked with some symbols. By the number and the intensity ratio of the peaks, the symmetry of the carbon cage and the dislocation of the metal atom from the symmetry axis or the symmetry plane can be determined. For C$_{82}$ cages, there are nine isomers that satisfy the isolated pentagon rule (IPR): C_2(1), C_s(2), C_2(3), C_s(4), C_2(5), C_s(6), C_{3v}(7), C_{3v}(8), and C_{2v}(9).[10] Figure 3a shows the ^{13}C NMR spectrum of Tm@C$_{82}$(I). The integrated intensity ratio of the peaks marked with a solid circle and an open square is 2:1, and the numbers of them are 38 and 6, respectively. Thus, the symmetry of Tm@C$_{82}$(I) was found to be C_s and there are four possible cages: three C_s isomers and C_{3v}(8). Three C_s cages clearly satisfy the ^{13}C NMR pattern, and the metal atom needs to be located in the symmetry plane. Moreover, if the metal atom is located in the symmetry plane and is displaced from the C_3 axis and the entire molecular symmetry becomes C_s, the C_{3v}(8) cage also satisfies the pattern because the C_{3v}(8) cage has six carbon atoms in the symmetry plane and 38 pairs of carbons on both sides of the symmetry plane. On the other hand, when the metal atom is located in the symmetry plane and is displaced from the C_3 or C_2 axis for the C_{3v}(7) or C_{2v}(9) cage, the molecular symmetry becomes C_s, but the number of peaks and the intensity ratio do not match the experimental results. Figure 3b shows the ^{13}C NMR spectrum of Tm@C$_{82}$(II). Its symmetry was found to be C_2 because the number of peaks whose intensities are almost the same is 41. The symmetry of the cage is C_2, and the metal atom needs to be located on the C_2 axis. Figure 3c shows the ^{13}C NMR spectrum of Tm@C$_{82}$(III). The intensity ratio of the peaks marked with a solid circle and an open square is 2:1, and the numbers of them are 17 and 7. Therefore the symmetry of Tm@C$_{82}$(III) was found to be C_{2v}; its cage is C_{2v}(9) (Figure 4), and the metal atom needs to be located on the C_2 axis. Our results also do not contradict an ab initio calculation.[11] Dunsch et al. assigned the symmetry of Tm@C$_{82}$ differently. They measured the spectra only in the range between 80 and 180 ppm, although we found additional signals out of this range.

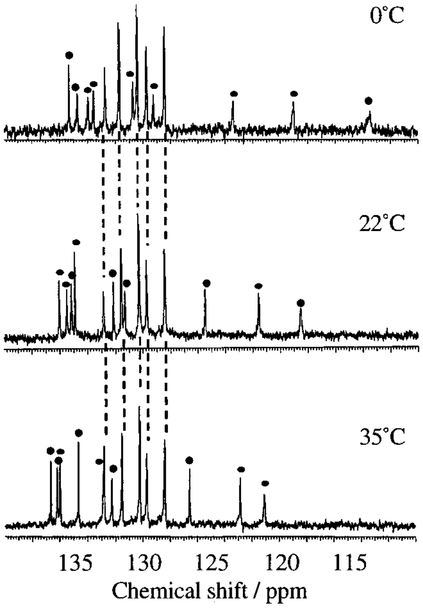

Figure 2. The temperature-dependent ^{13}C NMR spectra (125 MHz, CS$_2$) of Tm@C$_{82}$(II).

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(11) Ab initio calculation on Ca@C$_{82}$, which is also a divalent metallofullerene. Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **1997**, *274*, 226−230.

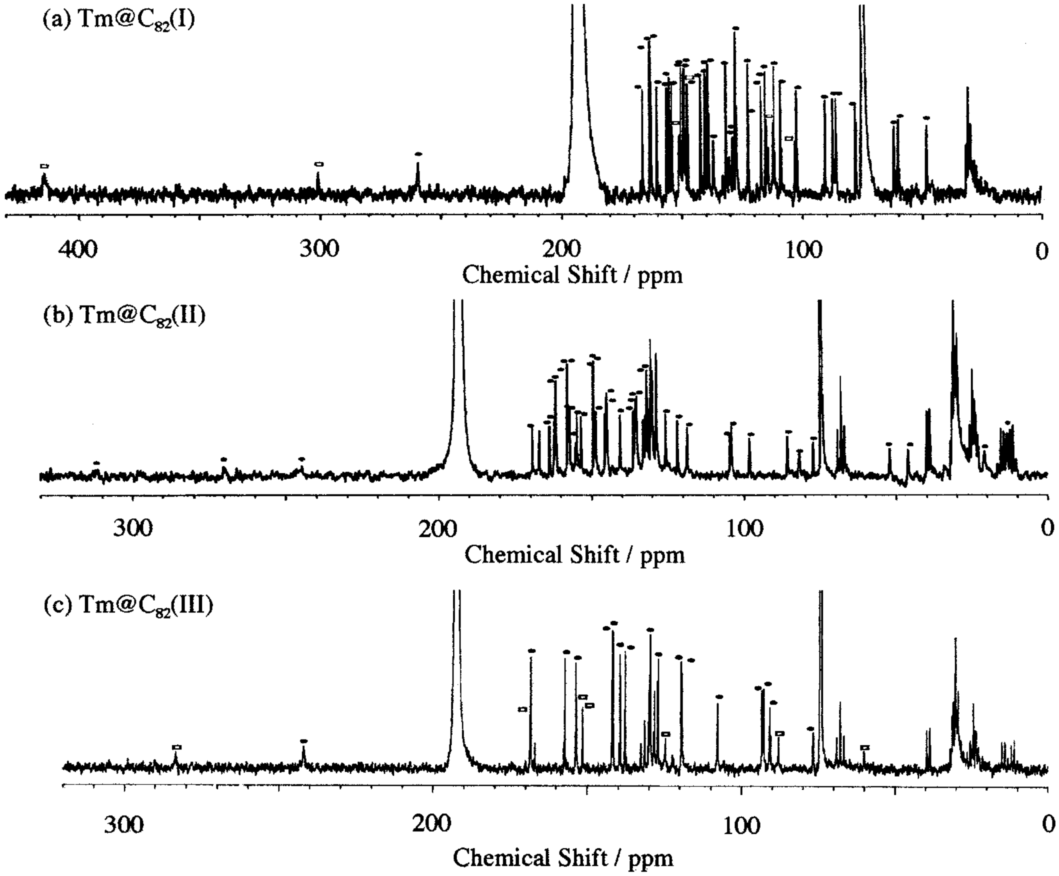

Figure 3. ^{13}C NMR spectra of (a) Tm@C_{82}(I), (b) Tm@C_{82}(II), and (c) Tm@C_{82}(III), measured at 125 MHz in CS_2 solvent with 5% 1,1,2,2,-tetrachloroethane-d_2 as an internal lock. The signals were accumulated for 3 or 4 days. The peaks marked with some symbols are assigned to Tm@C_{82}. In (a) and (c), the integrated intensity ratio of the peaks marked with a solid circle and an open square is 2:1. In (b), all the peaks marked with a solid circle have same intensity.

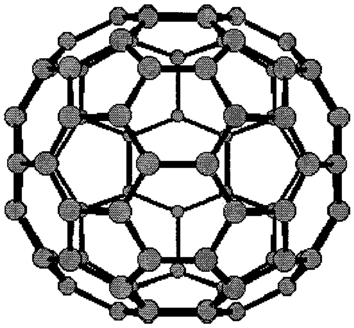

Figure 4. The structure of C_{82}(9) which is the cage of Tm@C_{82}(III).

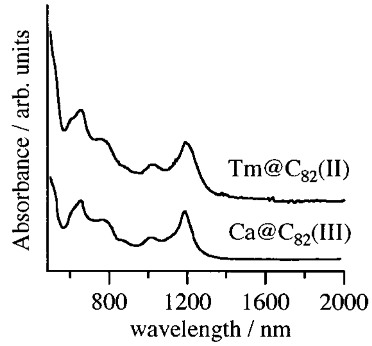

Figure 5. UV−vis−near IR absorption spectra of Tm@C_{82}(II) and Ca@C_{82}(III) in CS_2 solvent at room temperature. The latter is reproduced from ref 13, with permission from the publishers.

Discussion

Ca@C_{82} is a divalent metallofullerene[12] like Tm@C_{82}. Despite the difference in metal atoms, the absorption spectrum of Tm@C_{82}(II) is very similar to that of Ca@C_{82}(III) as shown in Figure 5. This has been supposed to indicate that not only are the oxidation states of the metal atoms identical, but the electronic transitions also mainly come from the π-electrons of the carbon cage. Therefore, the metallofullerenes whose absorption spectra resemble each other are considered to possess the same carbon cage. The symmetry of Ca@C_{82}(III) has been found to be C_2 by Shinohara et al.[13] On the other hand, we determined that the symmetry of Tm@C_{82}(II) is C_2. This coincidence of the cage symmetry strongly supports the above supposition. Strictly speaking, we cannot say that Tm@C_{82}(II) and Ca@C_{82}(III) have the same cage because there are three structural isomers with C_2 symmetry; even so, it is very plausible that the two metallofullerenes possess identical cages.

La@C_{82} is a trivalent metallofullerene, and thus the electronic structure of La@C_{82} is La^{3+}@C_{82}^{3-}. Due to an unpaired electron on the carbon cage, the relaxation time of ^{13}C nuclear spins becomes so short that ^{13}C NMR signals cannot be observed. To overcome this difficulty, Akasaka et al. electrochemically

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[12] Xu, Z.; Nakane, T.; Shinohara, H. *J. Am. Chem. Soc.* **1996**, *118*, 11309−11310.

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reduced La@C$_{82}$ to make it diamagnetic, and they succeeded in obtaining the ^{13}C NMR spectrum of the La@C$_{82}$ anion. On the other hand, Tm@C$_{82}$ is a divalent metallofullerene, and so the electronic structure of Tm@C$_{82}$ is Tm^{2+}@C$_{82}$$^{2-}$, and no unpaired electron exists on the carbon cage. However, Tm^{2+} has a 4f^{13} electronic structure; thus,the unpaired electron exists on the metal atom inside the cage. This unpaired electron affects the local magnetic field and the relaxation time for ^{13}C nuclear spins on the carbon cage. The peaks of Tm@C$_{82}$(II) (Figure 3b) are distributed over a very wide range compared to those of Ca@C$_{82}$ (130−150 ppm),[13] and the peaks of Tm@C$_{82}$ show temperature-dependent shifts, as is typical of paramagnetic metal complexes.[14−16]

Last, we compare the molecular structure of Tm@C$_{82}$ with that of La@C$_{82}$. Akasaka et al. reported that the symmetry of La@C$_{82}$ was C_{2v}.[7] Therefore we can conclude that La@C$_{82}$ and Tm@C$_{82}$(III) have an identical cage because there is only one isomer with C_{2v} symmetry as mentioned in the results section. This consequence confirms the suggestion by Sueki et al., which states that isomer III of divalent metallofulerenes has the same cage as the trivalent metallofullerene.[8,9] Quite recently, Akasaka et al. measured the ^{13}C NMR of the minor isomer of La@C$_{82}$ and determined its symmetry is C_s.[17] Although its symmetry C_s coincides with that of Tm@C$_{82}$(I), we cannot know the coincidence of the cage structure from only the results of ^{13}C NMR because there are four possible cages for Tm@C$_{82}$(I). Thus, X-ray studies of them are desirable.

Conclusions

Three isomers of Tm@C$_{82}$ were isolated, and the ^{13}C NMR spectra of them were measured. The symmetries of isomer I, II, and III were found to be C_s, C_2, and C_{2v} respectively. As a result, it was revealed that Tm@C$_{82}$(III) has an identical cage with La@C$_{82}$.

Acknowledgment. This work was partly supported by a grant from the Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: HPLC chromatograms, ^{13}C NMR spectra of Tm@C$_{82}$(II) in a proton-coupled mode and in a proton-decoupled mode, temperature dependent ^{13}C NMR spectra of Tm@C$_{82}$(II), absorption spectra, ESR spectra of three Tm@C$_{82}$ isomers, line positions and relative intensities in the ^{13}C NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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