

Characterization of Ce@C₈₂ and Its Anion

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Abstract: Ce@C₈₂ is isolated by high-performance liquid chromatography (HPLC) and the cage symmetry is determined as C_{2v} by measuring the ¹³C NMR spectra of its anion. The ¹³C NMR peaks of [Ce@C₈₂]⁻ show temperature-dependent shifts ascribed to the f electron remaining on the Ce atom. Both Ce@C₈₂ and [Ce@C₈₂]⁻ are silent in electron spin resonance spectroscopy (ESR) because of the highly anisotropic g matrix as well as of the fast relaxation process originating from the orbital angular momentum of the f electron. This is the complementary relationship to the observation of the paramagnetic shift in ¹³C NMR. [Ce@C₈₂]⁻ has lower stability in air than [La@C₈₂]⁻.

Introduction

Endohedral metallofullerenes (fullerenes with metal atoms encapsulated inside hollow carbon cages) have attracted special interest as new spherical molecules because they have unique properties that are not seen in empty fullerenes.¹ Among these, La@C₈₂ has been recognized as a prototype of endohedral metallofullerenes since its first extraction in 1991 by Smalley and co-workers.² We have verified that the carbon cages of the major (La@C₈₂-A) and minor (La@C₈₂-B) isomers of La@C₈₂ have C_{2v}³ and C_s⁴ symmetry, respectively, by analysis of the ¹³C NMR spectra of their anions. The C_{2v} structures of the major isomers, Sc@C₈₂-A and La@C₈₂-A, have been predicted by theoretical calculations⁵ and then confirmed by an X-ray powder

diffraction study via the maximum entropy method.^{6,7} Much attention has been paid to the electronic and magnetic properties of endohedral metallofullerenes having f electrons such as Ce@C₈₂,⁸ Pr@C₈₂,⁹ Tm@C₈₂,¹⁰ Gd@C₈₂,¹¹ and so forth. The existence of a spin–spin interaction between the carbon cage and the metal has been proposed. Meanwhile, we have isolated two isomers of Pr@C₈₂ by an efficient high-performance liquid chromatography (HPLC) separation system^{9b} and succeeded very recently in determining the structure of Pr@C₈₂-A on the basis of ¹³C NMR measurements of its anionic form.^{9c} On the other hand, Yang and co-workers^{8a} reported the isolation and

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X-ray photoelectron spectroscopy (XPS) study of Ce@C₈₂ and found that its visible and near-infrared (vis–NIR) absorption spectra correspond well to those of La@C₈₂-A. This spectral similarity suggests that Ce@C₈₂ and La@C₈₂-A have a common C₈₂ cage and an open-shell electronic structure. Iwasa and co-workers^{8b} reported the magnetic characteristics of Ce@C₈₂. Structural information on M@C₈₂ (M = lanthanide atom) with different metals provides an important clue to the mechanisms of formation and can be used for the development of new routes to the bulk production of endohedral metallofullerenes. In this context, it is of interest to determine the structures of a series of M@C₈₂ compounds. We report here the full characterization of Ce@C₈₂ and its anion.

Experimental Section

Soot-containing metallofullerenes were produced by the standard arc vaporization method with a composite anode containing graphite and cerium oxide in an atomic ratio of Ce/C ≈ 0.08. The composite rod was then subjected to an arc discharge as an anode under a helium atmosphere of 50 Torr. The raw soot was collected and extracted with 2,4,6-trichlorobenzene (TCB) at its boiling temperature for 16 h. The soluble fraction was injected into the HPLC; a PBB column (φ20 mm × 250 mm; Cosmosil, Nacalai Tesque Inc.) was used in the first step and a PYE column (φ20 mm × 250 mm × 2; Cosmosil, Nacalai Tesque Inc.) in the second step. Chlorobenzene and toluene were used for the mobile phases, respectively.

Electrochemical-grade tetrabutylammonium perchlorate (TBAP), purchased from Wako, was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. 1,2-Dichlorobenzene (ODCB) was distilled over P₂O₅ under vacuum prior to use. Visible and NIR absorption spectra were recorded on a Perkin-Elmer Lambda 19.

Bulk controlled-potential electrolysis^{3,4} of Ce@C₈₂ was used to prepare its anion with a potentiostat/galvanostat (BAS CW-50). Solutions containing [Ce@C₈₂][−] were obtained in ODCB containing 0.2 M TBAP by setting the applied potential at 150–250 mV more negative than the E_{1/2} value for the Ce@C₈₂/[Ce@C₈₂][−] redox couple.^{8c} The electrogenerated [Ce@C₈₂][−] was then transferred from the bulk cell to a 1.0 cm quartz cuvette under an argon atmosphere. Vis–NIR measurements were carried out under an Ar atmosphere.

The sample (~2 mg) prepared by bulk electrolysis was dried under vacuum and dissolved in carbon disulfide and deuterated tetrahydrofuran (THF-*d*₈) (1:1) under an Ar atmosphere. The ¹³C NMR spectra were measured at 125 MHz on a Bruker DRX500 spectrometer with a CryoProbe system. Chemical shifts were expressed downfield of the signals for the carbon atom of carbon disulfide as the internal standard (δ = 195.0). Some peaks were split into two or more peaks and/or broadened when the ¹³C NMR measurement was performed without proton decoupling. This means that these peaks originate from the carbon atoms in the molecules containing protons; therefore, these carbons were assigned to impurities.

Electron spin resonance (ESR) measurements were performed at room temperature and 1.5 K on a Bruker E500 spectrometer combined with a helium flow cryostat (Oxford Instruments Model ES910).

Results and Discussion

1. Stability of Ce@C₈₂. The absorption spectrum and redox property of Ce@C₈₂ are very similar to those of La@C₈₂, thus indicating the open-shell character of Ce@C₈₂.^{8b,c} This means that Ce@C₈₂ may be as sensitive to air as La@C₈₂; it is well-known that the ESR signal of La@C₈₂ decreases in the presence of air. Therefore, we first examined the stability of Ce@C₈₂ in air. Figure 1 shows the absorption spectra of Ce@C₈₂ in air and the dark. The absorption of Ce@C₈₂ starts to monotonically decrease within a week, which shows that Ce@C₈₂ is also air-

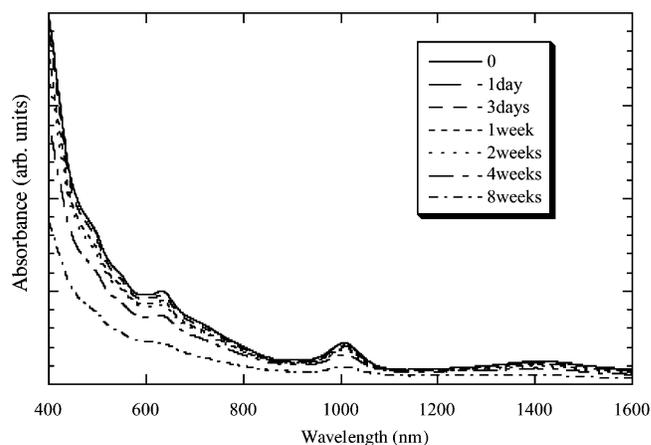


Figure 1. Changes in the vis–NIR absorption spectrum of Ce@C₈₂ in the air (in arbitrary units).

sensitive. We next examined the thermal and photochemical stabilities of Ce@C₈₂ in the absence of air. A degassed solution of Ce@C₈₂ in 1,2-dichlorobenzene at 293 K was heated in a sealed tube at 443 K for 60 min or photoirradiated over 400 nm (cut off <400 nm). In both cases, the absorption spectrum remained unchanged. When the solution was irradiated over 300 nm (cut off <300 nm), the absorption spectrum immediately became featureless. These results indicate that the stability of Ce@C₈₂ is similar to that of La@C₈₂.

2. Structure of Ce@C₈₂. Yang and co-workers^{8a} reported that the Ce atom in Ce@C₈₂ donates three valence electrons to the carbon cage, which results in formation of an open-shell electronic structure, formally described as Ce³⁺C₈₂^{3−}. For this reason, it is very difficult to determine the cage structure by ¹³C NMR measurements, because of its paramagnetic nature. Recently, we reported the structural determination of paramagnetic metallofullerenes such as La@C₈₂-A, La@C₈₂-B, and Pr@C₈₂-A by ¹³C NMR measurements of their anionic forms.^{3,4,9c} In this context, we carried out the reduction of Ce@C₈₂ to form a diamagnetic carbon cage metallofullerene anion and determined the cage structure by means of ¹³C NMR measurements of its anionic form.

A significant color change from dark brown to dark green was observed during the reduction of Ce@C₈₂. [Ce@C₈₂][−] has the onset of a band around 1600 nm with a near-IR band at 946 nm and a broad visible band at 611 nm (Figure 2). The anion is stable under an Ar atmosphere. However, [Ce@C₈₂][−] began to be oxidized within a week and returned to the neutral form in air and the dark (Figure 3). There is an isosbestic point between [Ce@C₈₂][−] and Ce@C₈₂, though the half-time period of Ce@C₈₂ in air is similar to that of [Ce@C₈₂][−]. This means that [Ce@C₈₂][−] is more sensitive to air than Ce@C₈₂. This is in contrast with the case of the La@C₈₂-A anion that is highly stable in air.³ We also examined the stability of [Ce@C₈₂][−] in the absence of air. A degassed solution of [Ce@C₈₂][−] in 1,2-dichlorobenzene was heated in a sealed tube at 443 K for 60 min or photoirradiated over 400 nm (cut off <400 nm) at 293 K. In both cases, the absorption spectrum remained unchanged. When the solution was irradiated over 300 nm (cut off <300 nm), the absorption spectrum immediately became featureless. The absorption spectrum of [Ce@C₈₂][−] remained unchanged not only in water but also in an ODCB solution of phenol (pK_a = 10), thiophenol (pK_a = 8), *p*-nitrophenol (pK_a = 7), acetic

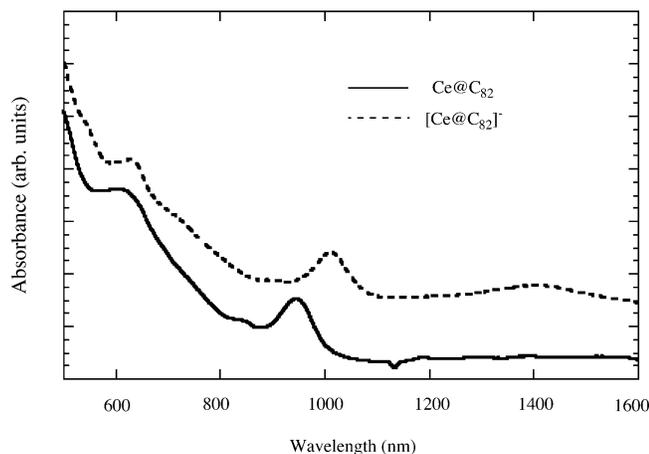


Figure 2. Vis-NIR absorption spectra of Ce@C₈₂ and [Ce@C₈₂]⁻.

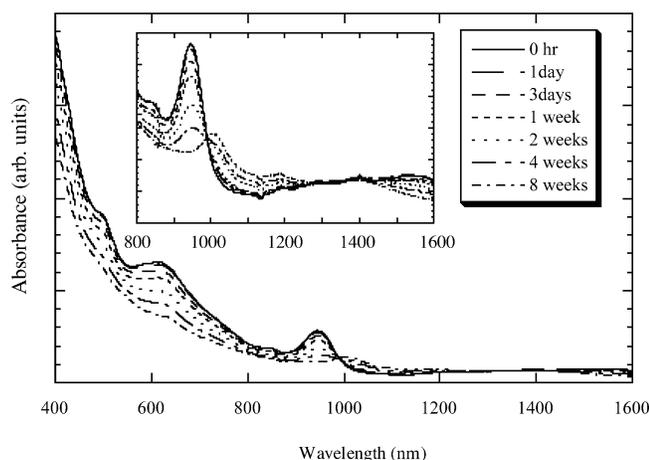


Figure 3. Changes in the vis-NIR absorption spectrum of [Ce@C₈₂]⁻ in the air (in arbitrary units).

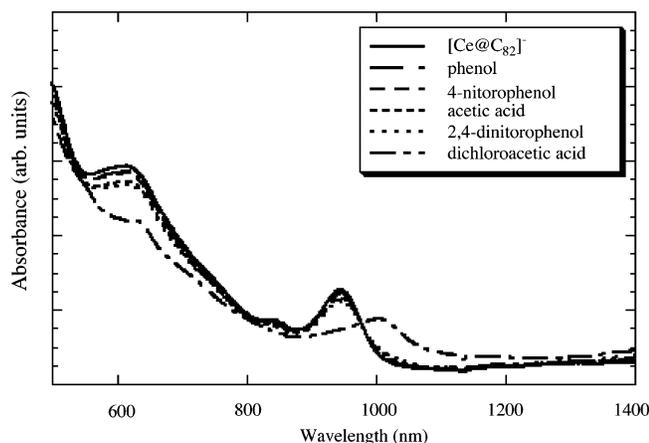


Figure 4. Vis-NIR absorption spectra of [Ce@C₈₂]⁻ in an *o*-dichlorobenzene solution in the presence of organic acids.

acid ($pK_a = 5$), or 2,4-dinitrophenol ($pK_a = 4$). [Ce@C₈₂]⁻ was oxidized to give Ce@C₈₂ in an ODCB solution of dichloroacetic acid ($pK_a = 1$).¹³ This may suggest that [Ce@C₈₂]⁻ survives even in an acidic solution ($pK_a = 4$) (Figure 4).

Because of the difficulty in preparing the single crystals of endohedral metallofullerenes, NMR measurements are generally

the best means for structural determination, but this technique could not be utilized for Ce@C₈₂ because of the paramagnetic nature of the carbon cage. On the other hand, the high stability of [Ce@C₈₂]⁻ and the diamagnetic nature of its carbon cage have enabled an NMR determination of the structure of Ce@C₈₂ by an analysis of the anion.

The C₈₂ fullerene has nine distinct isomers [*C*_{3*v*}(a), *C*_{3*v*}(b), *C*_{2*v*}, *C*₂(a), *C*₂(b), *C*₂(c), *C*_s(a), *C*_s(b), and *C*_s(c)] that satisfy the isolated pentagon rule.^{14,15} The ¹³C NMR of C₈₂ shows that only one isomer with *C*₂ symmetry is abundantly produced.¹⁶ It was once assumed that the metal in endohedral complexes, e.g., La in La@C₈₂, was encapsulated inside the abundant *C*₂ isomer. However, encapsulation of La in the *C*_{2*v*}, *C*_{3*v*}(b), or *C*_s(c) isomer can be substantially stabilized by a three-electron transfer from La to C₈₂, giving three possible endohedral structures with *C*_{2*v*}, *C*_{3*v*}, and *C*_s symmetry.⁵ In fact, we recently verified that the carbon cages of M@C₈₂-A (M = La, Pr) and La@C₈₂-B have *C*_{2*v*} and *C*_s symmetry, respectively.^{3,4,9c} Since three electrons are also transferred from Ce to C₈₂ in Ce@C₈₂,^{8b} it is likely that the endohedral structures also have *C*_{2*v*}, *C*_{3*v*}, and/or *C*_s symmetry, as is the case for La@C₈₂. The structures with *C*_{2*v*}, *C*_{3*v*}, and *C*_s symmetry have 24 [17(4) + 7(2)], 17 [11(6) + 5(3) + 1(1)], and 44 [38(2) + 6(1)] nonequivalent carbons, respectively, the values in parentheses being the relative intensities. As Figure 5 shows, the 125 MHz ¹³C NMR spectrum of [Ce@C₈₂]⁻ exhibits a total of 24 distinct lines (17 lines of nearly equal intensity and 7 lines of half intensity), verifying that Ce@C₈₂ has *C*_{2*v*} symmetry. This accords with theoretical calculations showing that the *C*_{2*v*} structure is the most stable.⁵

Although [Ce@C₈₂]⁻ and [La@C₈₂-A]⁻ have *C*_{2*v*} cage structures, we have observed two distinctive differences in their ¹³C NMR spectra. The carbon signals of [Ce@C₈₂]⁻ are observed between 110 and 170 ppm, whereas the signals of [La@C₈₂-A]⁻ appear between 135 and 165 ppm. We also observed the broadening of several carbon signals for [Ce@C₈₂]⁻. This kind of line broadening is not observed for [La@C₈₂-A]⁻. Though La³⁺ does not have an *f* electron on the metal, Ce³⁺ has a 4*f*¹ electronic structure. Thus the unpaired electron on the metal atom exists inside the carbon cage. This unpaired electron affects the local magnetic field and the fast relaxation of ¹³C nuclear spin on the carbon cage. So these differences are probably ascribed to the *f* electron remaining on the Ce atom.¹⁷ A similar effect of *f*-electron magnetism has also been observed for Tm@C₈₂¹⁰ and [Pr@C₈₂-A]^{-9c}

To shed light on the details of the effect of *f*-electron magnetism, we carried out low-temperature ¹³C NMR measurements. Figure 6 shows the ¹³C NMR spectra at 313–293 K. Some peaks of [Ce@C₈₂]⁻ showed temperature-dependent shifts, as is typical of a paramagnetic metal complex. However, these temperature-dependent shifts are much smaller than those of Tm@C₈₂, as reported by Kodama et al.¹⁰ One of the reasons for the large shift in ¹³C NMR of Tm@C₈₂ is that the Tm atom may locate closer to the carbon cage than the Ce atom^{8f} since the Tm²⁺ ion is much smaller than the Ce³⁺ ion. We find that some peaks undergo the larger temperature-dependent shifts in

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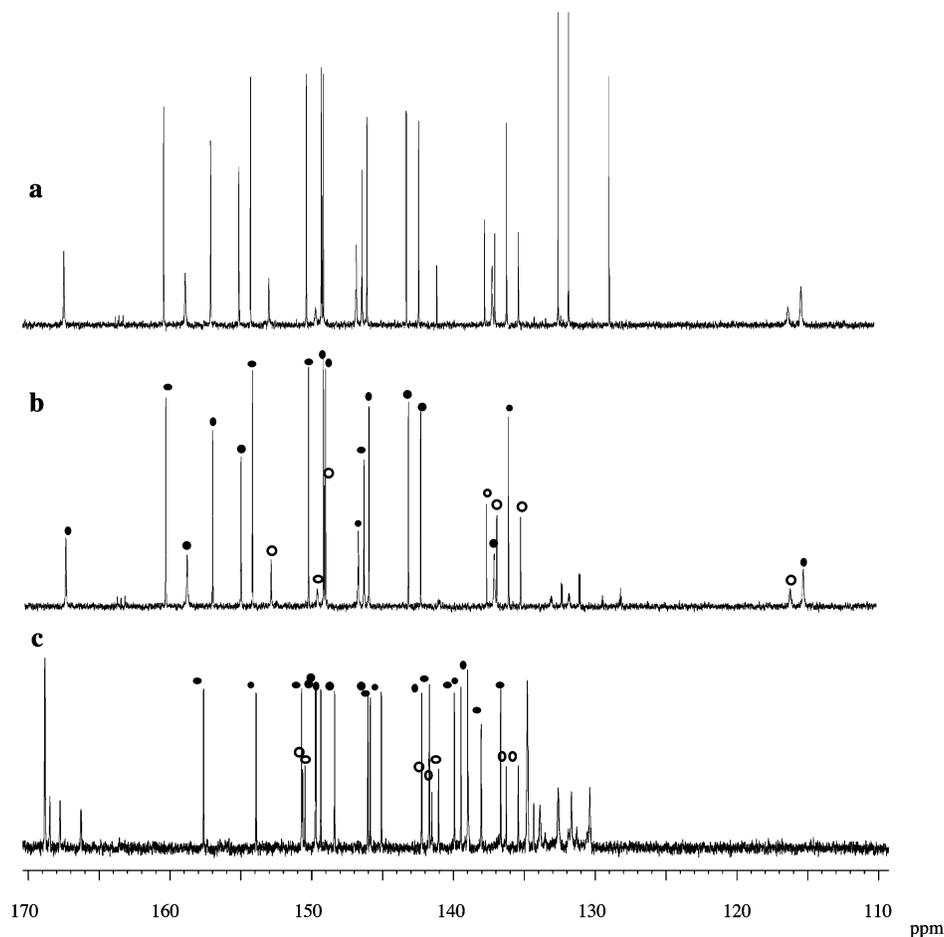


Figure 5. ^{13}C NMR of $[\text{Ce}@\text{C}_{82}]^-$, (a) with ^1H decoupling and (b) without ^1H decoupling (303 K), and (c) ^{13}C NMR of $[\text{La}@\text{C}_{82}\text{-A}]^-$ without ^1H decoupling (300 K). The 24 marked peaks with intensities 4 (●) and 2 (○) correspond to $[\text{Ce}@\text{C}_{82}]^-$. Line positions (ppm) are 165.02(2), 156.86(2), 156.16(2), 153.77(2), 152.38(2), 150.77(2), 149.45(1), 147.29(2), 146.95(1), 146.12(2), 145.93(2), 145.48(1), 143.52(2), 143.26(2), 142.79(2), 139.58(2), 138.64(2), 134.34(1), 133.92(2), 133.19(1), 133.14(2), 131.97(1), 112.52(1), 111.05(2).

all the other peaks. Therefore, these peaks must originate from the carbons nearest to the Ce metal. The different sign of paramagnetic shifts in Figure 6 may be caused by the anisotropic interaction of the dipole–dipole interaction. The fact that both $\text{Ce}@\text{C}_{82}$ and $\text{La}@\text{C}_{82}\text{-A}$ have the same C_{2v} carbon cage and the metals have the same oxidation state suggests that $\text{Ce}@\text{C}_{82}$ has an endohedral structure similar to that of $\text{La}@\text{C}_{82}\text{-A}$. $\text{La}@\text{C}_{82}\text{-A}$ has 12 C atoms nearer the La atom as shown in Figure 7. Because $\text{La}@\text{C}_{82}\text{-A}$ has C_{2v} symmetry, the 12 carbons show four signals [two signals with the intensity 4 (carbons A and C) and two signals with the intensity 2 (carbons B and D)] in the ^{13}C NMR spectrum. Since $\text{Ce}@\text{C}_{82}$ has also C_{2v} symmetry, the two most shifted peaks with an intensity of 4 (marked with asterisks in Figure 6) originate from carbons A and C, and the two most shifted peaks with intensity 2 (marked with plus signs in Figure 6) originate from carbons B and D.

3. ESR Spectra of $\text{Ce}@\text{C}_{82}$ and Its Anion. To characterize the electronic properties of $\text{Ce}@\text{C}_{82}$ and its anion, we carried out ESR measurements for both oxidation states. However, no ESR signal was observed at room temperature and 1.5 K. As mentioned earlier, adding one electron electrochemically, which allows a ^{13}C NMR measurement, closes the open-shell electronic structure of the C_{82} cage. On the other hand, whether $\text{Ce}@\text{C}_{82}$ is electrochemically reduced or not, one electron remains on the 4f orbital of Ce^{3+} ion. The remaining 4f electron produces an orbital angular momentum $L = 3$. The ground electronic

state of Ce^{3+} in the fullerene cage is supposed to be $^2F_{5/2}$ according to the literatures.¹⁸ Then the ESR signal would be characterized by a highly anisotropic g tensor, and the spectrum is broadened over the wide range of magnetic field. In addition to the anisotropic g tensor, the orbital angular momentum $L = 3$ reflects the fast relaxation process of the electron spin flip-flop, which accelerates the decay of the electron spin energy and the randomization of the aligned electron spin state. These might be the reason for the lack of ESR-detected absorption. In many cases of lanthanide metal endofullerenes, i.e., $\text{Ce}@\text{C}_{82}$, $\text{Pr}@\text{C}_{82}$, $\text{Nd}@\text{C}_{82}$, $\text{Sm}@\text{C}_{82}$, $\text{Dy}@\text{C}_{82}$, $\text{Ho}@\text{C}_{82}$, or $\text{Er}@\text{C}_{82}$, no ESR signal has been observed because of the remaining orbital angular momentum due to 4f electrons.

4. Reaction of $\text{Ce}@\text{C}_{82}$. We have already achieved chemical derivatization of the major isomers of the endohedral metallofullerenes such as $\text{La}@\text{C}_{82}$, $\text{Pr}@\text{C}_{82}$, and $\text{Gd}@\text{C}_{82}$, giving exohedral adducts.^{20,9b} This study has been extended here to understand whether there is any significant difference in chemical reactivity between $\text{La}@\text{C}_{82}\text{-A}$ and $\text{Ce}@\text{C}_{82}$; these have the same cage (C_{82} C_{2v}) and electronic structure ($\text{M}^{3+}\text{C}_{82}^{3-}$) but have different metals inside the carbon cage. A solution of

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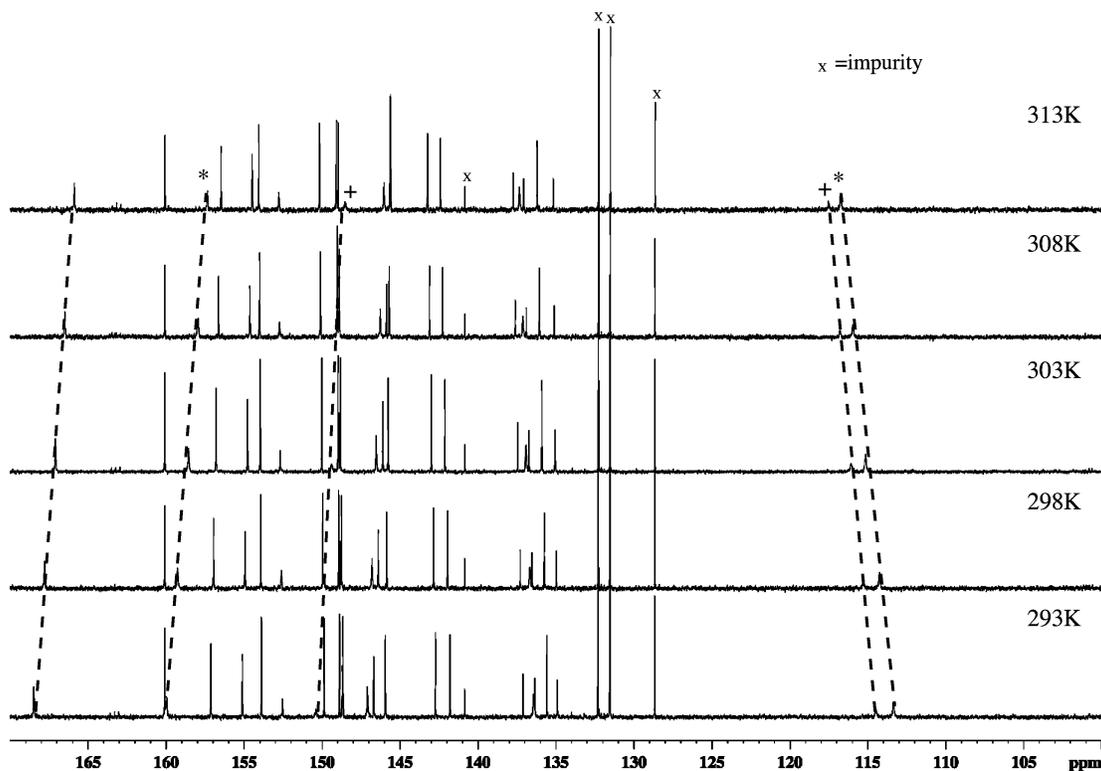


Figure 6. Temperature-dependent ¹³C NMR spectra of [Ce@C₈₂]⁻.

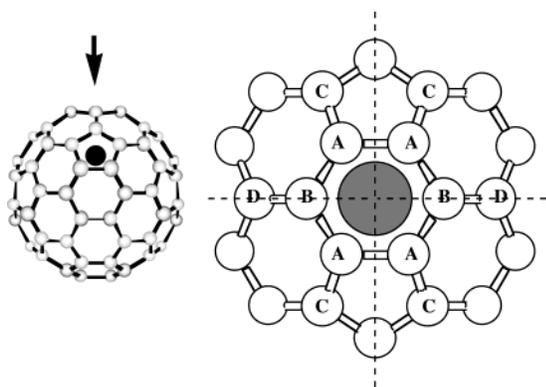


Figure 7. Structure of La@C₈₂-A (C_{2v}).

Ce@C₈₂ and 1,1,2,2-tetramesityl-1,2-disilirane in 1,2,4-trichlorobenzene was photoirradiated at 293 K with a tungsten-halogen lamp (cutoff <400 nm) in a degassed sealed tube. The formation of the 1:1 adduct of Ce@C₈₂ with disilirane was confirmed by fast atom bombardment (FAB) mass analysis. The thermal reaction of Ce@C₈₂ with disilirane at 353 K also provided the corresponding 1:1 adduct. Nearly identical results have been obtained with La@C₈₂-A. Empty fullerenes, such as

C₆₀, C₇₀, C₇₆, or C₇₈, react photochemically with disilirane but not thermally.¹⁹ Thus the observed high chemical reactivities of Ce@C₈₂ with disilirane can be rationalized by the strong ability as an electron donor and acceptor as compared with empty fullerenes such as C₆₀.¹⁹ This is consistent with the fact that Ce@C₈₂ has lower oxidation and reduction potentials than C₆₀.

Conclusions

Ce@C₈₂ has been isolated, and the ¹³C NMR spectra of its anion have been measured. The NMR spectra show that Ce@C₈₂ has a C_{2v} cage structure, as do La@C₈₂-A, Pr@C₈₂-A, and Ce@C₈₂. The ¹³C NMR spectra of [Ce@C₈₂]⁻ show temperature-dependent shifts ascribed to the f electron remaining on the Ce atom. This kind of temperature-dependent shift is observed for the first time in the [M@C₈₂]⁻ system.

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Supporting Information Available: Cyclic voltammogram of Ce@C₈₂ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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