

# A C<sub>82</sub> Carbon Cage Stable toward Two Different Oxidation States of Endohedral Metal Atoms

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The effect of transmutation of a metallic element encaged in C<sub>82</sub> through EC radioactive decay was studied for the <sup>146</sup>Gd → <sup>146</sup>Eu → <sup>146</sup>Sm decay series. The metallofullerene containing the EC decay progeny <sup>146</sup>Eu was found chemically stable and eluted in a HPLC separation at a retention time which corresponded to the retention time of one of the minor isomers of Eu@C<sub>82</sub>(3). As the oxidation state of the metal atom in Gd@C<sub>82</sub> and Eu@C<sub>82</sub> is known to be +3 and +2, this result suggests that the C<sub>82</sub> cage which forms a chemically stable metallofullerene with the metal atom at the +3 oxidation state can also form a stable metallofullerene with a metal atom at the +2 oxidation state.

## Introduction

Since the publication of reports on a simple method for the production and isolation of large quantities of metallofullerenes,<sup>1–3</sup> their properties have been both intensively and extensively studied. But some important facts on the nature of the metal atoms and on the carbon cages have only recently been unveiled. For example, the endohedral nature of metallofullerenes was confirmed by a synchrotron X-ray powder diffraction study of Y@C<sub>82</sub>;<sup>4</sup> a strong charge-transfer interaction between La<sup>3+</sup> and C<sub>82</sub><sup>3–</sup> was suggested by an electron-spin resonance study,<sup>5</sup> and the divalent oxidation state of the metal ions was indicated for Tm@C<sub>82</sub>,<sup>6,7</sup> Ca@C<sub>82</sub>,<sup>8</sup> Eu@C<sub>82</sub>, and Yb@C<sub>82</sub><sup>9</sup> by several investigators. For the C<sub>82</sub> carbon cage, 9 isomers, which obey the isolated pentagon rule, are predicted, and the C<sub>82</sub> cage produced by the arc discharge method is reported to have C<sub>2</sub> symmetry from both a <sup>13</sup>C NMR study<sup>10</sup> and theoretical considerations of the cage stability.<sup>11</sup> Several metallofullerenes were also reported to have isomers: for example, 4 isomers for Ca@C<sub>82</sub>,<sup>8</sup> 3 for Tm@C<sub>82</sub>,<sup>6</sup> Eu@C<sub>82</sub>, and Yb@C<sub>82</sub>,<sup>9</sup> and 2 for La@C<sub>82</sub><sup>12</sup> and Y@C<sub>82</sub>.<sup>13</sup> However, the reliable identification of carbon cages of metallofullerenes is still rarely reported except for the C<sub>80</sub> cage of La<sub>2</sub>@C<sub>80</sub>, which was deduced from the observed <sup>13</sup>C NMR data to have an I<sub>h</sub> symmetry.<sup>14</sup>

In a previous work, the specificity of a carbon cage toward a certain oxidation state of the metal atom for formation of a stable metallofullerene has been investigated by use of a β<sup>–</sup>-decaying nuclide as the encaged metal atom. The β<sup>–</sup> decay brings about an increase of the atomic number by one unit, and if the progeny nuclide is also radioactive, the HPLC behavior of the newly formed metallofullerene containing it can easily be traced by radioactivity monitoring. In the previous experiment, three kinds of β<sup>–</sup> decay series were studied: (1) <sup>161</sup>Gd → <sup>161</sup>Tb → <sup>161</sup>Dy,<sup>15</sup> (2) <sup>155</sup>Sm → <sup>155</sup>Eu → <sup>155</sup>Gd,<sup>16,17</sup> and (3) <sup>177</sup>Yb → <sup>177</sup>Lu → <sup>177</sup>Hf.<sup>16,17</sup> The results have shown that in the β<sup>–</sup> decay series 1 and 2 where the most stable oxidation state of the metal atom in the C<sub>82</sub> cage is expected to be the same for both the parent and daughter atom, namely, Gd(+3) → Tb(+3) and Sm(+2) → Eu(2+), the C<sub>82</sub> metallofullerenes of the eluted daughter atoms are found at the expected retention time in the HPLC elution. But in the decay series (3) where the most stable oxidation states in the C<sub>82</sub> cage of the parent and daughter

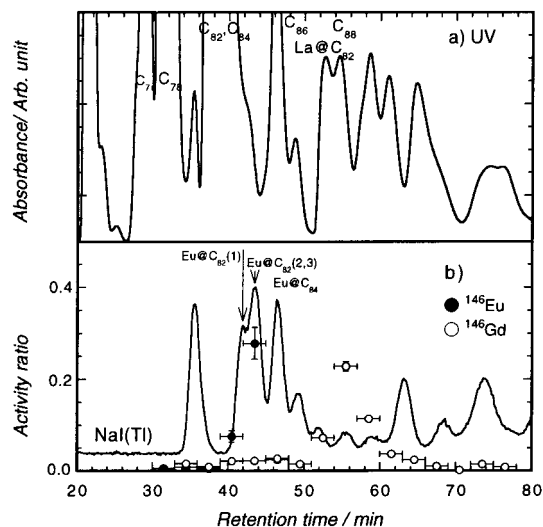
TABLE 1: Nuclear Data Relevant to the Present Study

isotope	half-lives	E <sub>EC</sub> /MeV (intensity)	E <sub>R</sub> (EC)/eV	E <sub>γ</sub> /keV (I <sub>γ</sub> /%)
<sup>146</sup> Gd	48.3 d	1.37 (77%)	6.4	114.7 (50.0%)
↓		1.52 (23%)	8.0	115.5 (50.0%) 154.6 (46.6%)
<sup>146</sup> Eu	4.58 d	3.878 <sup>a</sup>		747.2 (98.3%)
↓				
<sup>146</sup> Sm	1.03 × 10 <sup>8</sup> y			

<sup>a</sup> This value is Q<sub>EC</sub> of <sup>146</sup>Eu. E<sub>EC</sub>: EC transition energy. E<sub>γ</sub>: γ-ray energy. I<sub>γ</sub>: intensity of the γ-ray per decay in percentage.

atoms are different, namely, +2 for Yb and +3 for Lu, <sup>177</sup>Lu was not observed at the retention time for Lu@C<sub>82</sub> nor at the time for Yb@C<sub>82</sub> but at a much longer retention time which was found to coincide with the time for the chemical species of metallofullerene produced by heavy dose reactor irradiation. Thus, results of the previous work suggest that C<sub>82</sub> carbon cages that form stable metallofullerenes with metal atoms at +2 oxidation are not the stable cage for atoms at the +3 oxidation state.

In the present work, the effect of transmutation of an encaged metal atom on the stability of M@C<sub>82</sub> is studied for the <sup>146</sup>Gd → <sup>146</sup>Eu → <sup>146</sup>Sm EC decay series. As it is known that Gd atoms in the M@C<sub>82</sub> metallofullerene take the +3 oxidation state<sup>5</sup> while Eu atoms take the +2 oxidation state,<sup>9</sup> the most stable oxidation state of the metal atom in C<sub>82</sub> is expected to change from +3 to +2 after EC decay. The EC decay produces an inner-shell vacancy, but it is considered that the electron shake-off as a result of this vacancy is negligible since the effective charge for the outer-shell electrons remains essentially unchanged, as the decrease in nuclear charge is compensated by a change in shielding.<sup>18</sup> Therefore, like the case of β<sup>–</sup> decay in which the electron shake-off process actually provides no excitation, the electronic perturbation caused by the EC decay process itself can be ignored. The K-shell fluorescence yield for Eu is 0.93, and the probability for the Auger effect which is the main cause of atomic excitation following EC decay is at most only 7%. Some relevant nuclear data of this EC-decay series are given in Table 1. The recoil energies of <sup>146</sup>Eu are calculated to be 6.4 (77%) and 8.0 eV (23%), corresponding to the two possible EC transitions which are too small to break chemical bonds.



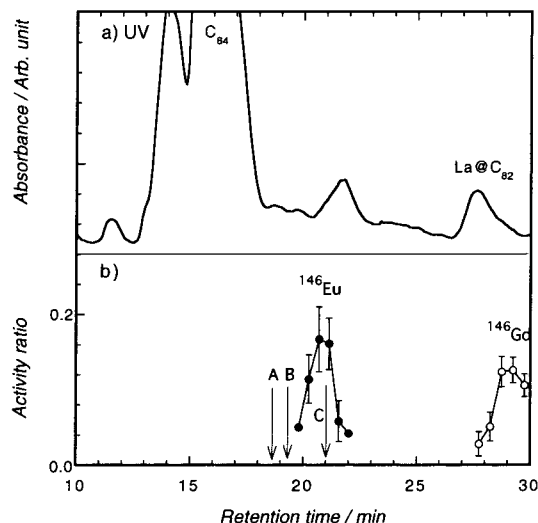
**Figure 1.** Elution curves of the  $^{146}\text{Gd}$  crude sample (Buckyprep column (10 mm  $\phi$   $\times$  250 mm), toluene as eluent, flow rate 3.2 mL  $\text{min}^{-1}$ ). (a) Elution curve observed by on-line monitoring with UV absorption at 340 nm. (b) Elution curves for  $^{146}\text{Gd}$  (open points) and  $^{146}\text{Eu}$  (filled points) observed by measuring  $\gamma$ -ray counts by a HPGe detector in each eluted fraction. Elution curve shown by the solid line is the one obtained in the previous work by on-line monitoring with a NaI(Tl) detector of the Eu crude sample containing radioactive Eu isotopes.<sup>9</sup>

## Experimental Section

The  $^{146}\text{Gd}$  crude sample was produced by the conventional arc discharge of graphite rods containing radioactive  $^{146}\text{Gd}$  tracer and a large amount of La (C:La = 150:1) in a 400 Torr He-gas atmosphere followed by  $\text{CS}_2$  extraction.<sup>20</sup> Separation of the fullerene species was first performed by HPLC on 5PBB (Cosmosil, Nakalai Tesque Inc., 10 mm  $\phi$   $\times$  250 mm) columns with  $\text{CS}_2$  as the solvent and also by Buckyprep (Cosmosil, Nakalai Tesque Inc., 10 mm  $\phi$   $\times$  250 mm) with toluene. In the second experiment, the  $^{146}\text{Gd}@C_{82}$  fractions eluted from the Buckyprep column was left standing for 40 days and then injected into the Buckyclutcher I column (Regis Chemicals Corp., 10 mm  $\phi$   $\times$  250 mm) with a mixture of toluene and hexane (70:30) as the solvent. The elution was monitored by an UV monitor by off-line  $\gamma$ -ray measurements and HPGe detection of eluted fractions.

## Results and Discussion

The results of the HPLC elution experiment for the  $^{146}\text{Gd}$  crude sample are presented in Figure 1. Figure 1a shows the HPLC elution monitored by UV absorption. Assignments of some peaks were made from our knowledge acquired in previous experiments.<sup>9</sup> In Figure 1b the elution of  $^{146}\text{Gd}$  (open points) and  $^{146}\text{Eu}$  (filled points) monitored by  $\gamma$ -ray measurements of elution fractions is shown. They were collected every 3 min during the retention time of 30–70 min. The radioactivities of  $^{146}\text{Gd}$  and  $^{146}\text{Eu}$  observed in each fraction were normalized to the total activity injected into the HPLC column. The lower solid curve of Figure 1b shows the elution curve observed for the Eu-crude sample with assignments of the elution peaks of  $\text{Eu}@C_{82}$  isomers as reported in our previous work.<sup>9</sup> Figure 1b shows that the peak of  $^{146}\text{Eu}$  is observed at the retention time (43 min) for  $\text{Eu}@C_{82}(2,3)$  isomers in which the Eu atom is considered to be in the +2 oxidation state.<sup>9</sup> The peak of  $^{146}\text{Gd}$  was observed at the retention time of 56 min, as expected for  $\text{Gd}@C_{82}$  with the Gd atom in the +3 oxidation state.<sup>9,21</sup> The observed radioactivity of  $^{146}\text{Eu}$  corresponded to almost 100%



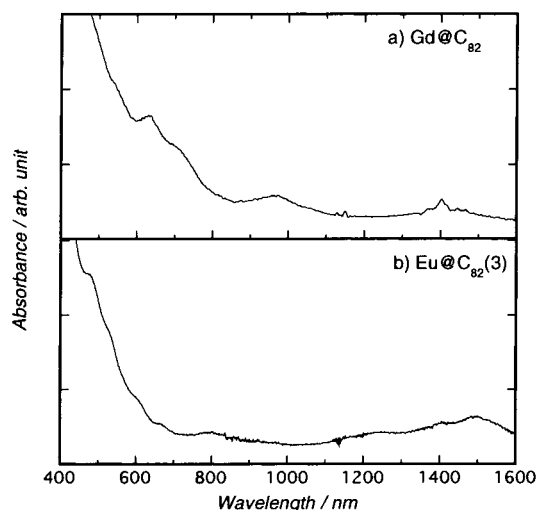
**Figure 2.** Elution curves of the  $^{146}\text{Gd}@C_{82}$  sample corresponding to the fractions under the  $^{146}\text{Gd}$  (open circles) in Figure 1b. A Buckyclutcher I column (10 mm  $\phi$   $\times$  250 mm) was used with a mixture of toluene and hexane (70:30) as the eluent at a flow rate of 2.0 mL  $\text{min}^{-1}$ . Elution curves observed by on-line monitoring with UV absorption at 340 nm (upper) and by  $\gamma$ -ray spectrometry of  $^{146}\text{Gd}$  (open points) and  $^{146}\text{Eu}$  (filled points) for the eluted fractions collected every minute by an HPGe detector (lower).

of the quantity expected from the radioactivity of the parent  $^{146}\text{Gd}$  isotope.

The results of the second experiment are plotted in Figure 2. Figure 2a shows the HPLC elution from the Buckyclutcher I column monitored by UV absorption. Elution fractions were collected every 1 min during the retention time of 15–30 min, and the  $\gamma$ -rays emitted from  $^{146}\text{Gd}$  and  $^{146}\text{Eu}$  were determined by an HPGe detector. The radioactivities of  $^{146}\text{Gd}$  and  $^{146}\text{Eu}$  observed in each fraction were normalized to those injected to the column and are shown by open and filled points, respectively, in Figure 2b. In the figure, the arrows indicate the positions (retention time) of the three isomers of  $\text{Tm}@C_{82}$  reported in ref 6.  $^{146}\text{Eu}$  is found eluted in the fraction corresponding to the peak of one of the  $^{146}\text{Eu}@C_{82}$  isomers, namely,  $\text{Eu}@C_{82}(3)$ , at the retention time of 21 min, which is the same retention time for the  $\text{Tm}@C_{82}(\text{C})$  isomer with the metal atom in +2 oxidation state. This retention time of  $^{146}\text{Eu}$  is clearly different from the retention time (28 min) for  $^{146}\text{Gd}$ , which coincides with the retention time for  $^{146}\text{Gd}@C_{82}$  in the +3 oxidation state.

The results of the two HPLC elution curves clearly show that the retention time differs for  $^{146}\text{Gd}@C_{82}$  and  $^{146}\text{Eu}@C_{82}$ . It is reminded that the  $^{146}\text{Eu}$  in the sample was produced from  $^{146}\text{Gd}$  in a  $C_{82}$  cage through EC decay. The present experiment showed, as mentioned above, that nearly 100% of the radioactivity of  $^{146}\text{Eu}$  expected from the decay of  $^{146}\text{Gd}$  was found to be eluted under the peak shown by the solid points in Figure 2b. Therefore,  $^{146}\text{Eu}$  remains in the  $C_{82}$  cage of the parent nuclide  $^{146}\text{Gd}$  although its oxidation state is changed from +3 of Gd to the +2 for Eu. It is to be noted that the +3 oxidation state for Gd in  $\text{Gd}@C_{82}$  and +2 state for  $\text{Eu}@C_{82}(3)$  are supported by the similarity of their UV-vis absorption spectra to those for  $\text{M}@C_{82}$  (M = Y and La)<sup>4,5</sup> and to those for  $\text{Tm}@C_{82}(\text{C})$ ,<sup>6</sup> respectively, whose oxidation states have been deduced by other physical means.

Recent theoretical calculations<sup>22</sup> predict the existence four stable cages for the formation of  $\text{M}@C_{82}$  with M in the +2 oxidation state and three cages for M in the +3 oxidation state, the cages with  $C_{2v}$  and  $C_s(\text{c})$  symmetry being the most stable



**Figure 3.** UV-vis absorption spectrum of (a)  $\text{Gd@C}_{82}$  and (b)  $\text{Eu@C}_{82}(3)$ . The samples were produced by the conventional arc discharge method and purified as described in ref 9.

ones for both the +2 and +3 atoms. However, the present work has revealed for the first time experimentally the existence of a  $\text{C}_{82}$  carbon cage that can form chemically stable metallofullerenes with the metal atoms at different oxidation states of +3 and +2. It is also proven that this carbon cage is the most commonly produced cage for +3 atoms and it is a minor isomer cage for +2 metal atoms. In our previous experiments,<sup>17</sup> it was shown that the production yield of this minor isomer for  $\text{Eu@C}_{82}$  is less than 10% of the total yield of the three isomers produced by the conventional arc discharge method. The existence of a  $\text{C}_{82}$  carbon cage that forms chemically stable metallofullerenes of both +2 and +3 metal atoms was actually also observed in our previous study of the  $\beta^-$ -decay series of  $^{177}\text{Yb} \rightarrow ^{177}\text{Lu} \rightarrow ^{177}\text{Hf}$  in  $\text{C}_{82}$  carbon cages, although no special attention was given to it in the previous paper.<sup>16</sup> The results indicated that when  $^{177}\text{Yb@C}_{82}$  in the +2 oxidation state decayed to  $^{177}\text{Lu}$ , most of the chemical species containing  $^{177}\text{Lu}$  were observed at a much later HPLC retention time than the time expected for  $\text{Lu@C}_{82}$  (Lu in +3 oxidation) and only a minor fraction of less than one-tenth was found eluted at the expected position for  $\text{Lu@C}_{82}$ . This experimental finding supports the existence of a special  $\text{C}_{82}$  cage which forms a chemically stable  $\text{M@C}_{82}$  metallofullerene both for metal atoms of the +2 and +3 oxidation states. That is, the experimental results can support the interpretation that only the minor isomer of  $\text{Yb@C}_{82}(3)$  (Yb in +2) produced by the arc method (the yield of less than 10%) gave a chemically stable  $\text{Lu@C}_{82}$  (Lu in +3) after  $\beta^-$ -decay, and other major isomers of  $\text{Yb@C}_{82}(1)$ ,  $\text{Yb@C}_{82}(2)$  did not form chemically stable  $\text{Lu@C}_{82}$  as those carbon cages are different from the one used for  $\text{Lu@C}_{82}$  (Lu in +3).

In Figure 3a and b, the UV-vis absorption spectra observed for  $\text{Gd@C}_{82}$  and the minor isomer of  $\text{Eu@C}_{82}(3)$  are shown. The results of the present work suggest that the  $\text{C}_{82}$  carbon cage is the same for the two metallofullerenes, and the completely

different absorption spectra shown in Figure 3 originate from the difference in the charge state of the encaged metal atom.

## Conclusion

It is concluded that the existence of a special kind of  $\text{C}_{82}$  carbon cage that forms chemically stable metallofullerenes with metal atoms of both the +2 and +3 oxidation state is experimentally proven for the first time. This cage is the one which commonly forms  $\text{M@C}_{82}$  with M in the +3 state and the one which forms the minor isomer of  $\text{M@C}_{82}(3)$  (or  $\text{Tm@C}_{82}(\text{C})$ ) for M in the +2 oxidation state.

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