**Popular C_{82} Fullerene Cage Encapsulating a Divalent Metal Ion Sm^{2+}: Structure and Electrochemistry**

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†Supporting Information

**ABSTRACT**: Two Sm@C_{82} isomers have been well characterized for the first time by means of $^{13}$C NMR spectroscopy, and their structures were unambiguously determined as Sm@C_{82}(9)-C_{82} and Sm@C_{82}(7)-C_{82}, respectively. A combined study of single crystal X-ray diffraction and theoretical calculations suggest that in Sm@C_{82}(9)-C_{82} the preferred Sm^{2+} ion position shall be located in a region slightly off the C_{3} axis of C_{82}(9)-C_{82}. Moreover, the electrochemical surveys on these Sm@C_{82} isomers reveal that their redox activities are mainly determined by the properties of their carbon cages.

**INTRODUCTION**

Filling a fullerene cage with metals or a metallic cluster gives rise to the formation of endohedral metallofullerene (EMF). Such a concept has been developed a lot since the middle of the 1990s, when an EMF (i.e., La@C_{82}) was detected and simply characterized for the first time by means of laser fragmentation.\(^1\) In the past decade, a variety of EMFs have been synthesized, isolated, and characterized.\(^2,3\) Great interest has been devoted to their unique structures and favorable properties. Particularly, La@C_{82} and its analogous M@C_{82} (M = group 2−3 elements and most lanthanides), which are more abundantly produced relative to others, have been widely studied and exhibited potential applications in the fields of medicine and material science.\(^4,5\)

In contrast to the early discovery of La@C_{82}, its structure has remained unknown for a long time. The breakthrough was made by Nagase et al. in 1998.\(^6\) They predicted the major isomer of La@C_{82}(9)-C_{82} as well as the minor isomers of La@C_{82}(6)-C_{82} and La@C_{82}(7)-C_{82} via theoretical calculations.\(^6\) These predictions have been unambiguously confirmed by a number of subsequent studies of NMR and single crystal X-ray diffraction (XRD).\(^7−9\) The electronic structures of these isomeric La@C_{82} have been generally described using an electronic model of La^{3+}@C_{82}^{3−},\(^6\) suggesting a formal transfer of three electrons between the metal and cage. It was believed that such a metal-cage interaction can contribute to the stabilization of the isomeric C_{82} cages.

Furthermore, recent studies revealed that these isomeric C_{82} cages can be stabilized not only by a trivalent metal ion but also by a divalent metal ion such as Ca^{2+}, Tm^{2+}, Yb^{2+}, and Sm^{2+}. The structures of divalent M@C_{82} (M = Ca, Tm, Yb) have been characterized using XRD, NMR, and DFT calculations or a combination. Previous studies reported three isomers for Tm@C_{82}\(^10\) and Yb@C_{82}\(^11\) (i.e., C_{82}(9), C_{82}(5), and C_{82}(6) isomers) and four isomers for Ca@C_{82}\(^12\) (i.e., C_{82}(9), C_{82}(5), C_{82}(6), and C_{82}(7) isomers). Among them, the C_{82}(7) isomer of Ca@C_{82} was tentatively proposed based on an incomplete $^{13}$C NMR spectrum, and the C_{82}(8) isomer could not be fully excluded.

On the other hand, another divalent EMF Sm@C_{82} has been studied by three independent groups. It is noteworthy that different metal sources were used by these groups, and they reported different isomeric distributions of Sm@C_{82}. Specifically, three isomers were obtained by using Sm_{2}O_{3} as a samarium source, while four isomers were obtained by using SmNi_{2}/Sm_{2}Co_{17} alloy as a metal source.\(^13,14\) The three isomers reported by Liu et al. were characterized as Sm@C_{82}(5)-C_{82}, Sm@C_{82}(6)-C_{82}, and Sm@C_{82}(7)-C_{82} using single crystal
RESULTS AND DISCUSSION

Two Sm@C\textsubscript{82} isomers were prepared and isolated according to the previously reported procedure and characterized by MALDI-TOF mass and UV-vis-NIR spectroscopy (see Figures S1, S2).\textsuperscript{14a} One isomer was determined as Sm@C\textsubscript{2v}(9)-C\textsubscript{82} using a combined study of NMR and single crystal XRD. As shown in the proton decoupled or proton coupled $^{13}$C NMR spectrum (see Figure 1), 24 signals (17 with full intensity and seven with half) are clearly seen in the range of 190–110 ppm at 293 K. This pattern evidently corresponds to the C\textsubscript{2v}(9)-C\textsubscript{82} cage, which corroborates well with the previous assignment based on the UV-vis-NIR spectroscopic studies.\textsuperscript{14b} Moreover, summarizing all the previously reported $^{13}$C NMR spectra of M@C\textsubscript{2v}(9)-C\textsubscript{82} (i.e., [La@C\textsubscript{2v}(9)-C\textsubscript{82}]\textsuperscript{+}, [Y@C\textsubscript{2v}(9)-C\textsubscript{82}]\textsuperscript{+}, [Pr@C\textsubscript{2v}(9)-C\textsubscript{82}]\textsuperscript{+}, and Yb@C\textsubscript{2v}(9)-C\textsubscript{82}), the $^{13}$C signals of cage carbons are generally distributed in a narrow range (160–130 ppm) compared to those of Sm@C\textsubscript{2v}(9)-C\textsubscript{82}. It is noteworthy that there is no unpaired electron on the endohedral La\textsuperscript{3+}, Y\textsuperscript{3+}, Pr\textsuperscript{3+}, or Yb\textsuperscript{2+} ion, whereas Sm\textsuperscript{2+} has a 4f electronic structure, and thus, there are six unpaired f electrons on the endohedral Sm\textsuperscript{2+} ion. These unpaired electrons significantly affect the local magnetic field and the fast relaxation of $^{13}$C nuclear spins on the adjacent cage carbons, thus contributing to the NMR chemical shifts of these cage carbons.

Furthermore, the absolute structure of Sm@C\textsubscript{2v}(9)-C\textsubscript{82} was determined via a single-crystal XRD study. A cocystal of Sm@C\textsubscript{2v}(9)-C\textsubscript{82}/Ni\textsuperscript{II}(OEP) suitable for X-ray analysis was obtained by slow diffusion of a benzene solution of EMF into a CHCl\textsubscript{3} solution of Ni\textsuperscript{II}(OEP). The molecular structure was resolved and refined in a C\textsubscript{2}v/m (No. 12) space group.\textsuperscript{15} Both the cage and endohedral metal atom were found to be disordered. In particular, two cage orientations with fractional occupancies of 0.27 and 0.23, respectively, have been identified. Figure 2 shows the major cage orientation, the major samarium site (Sm1, 0.116 occupancy), and their relationships to Ni\textsuperscript{II}(OEP) moiety. The shortest C–Ni distance between a carbon ion of the major cage (C22B) and the Ni ion in Ni\textsuperscript{II}(OEP) was determined as 2.751(10) Å. This value is similar to those of 2.79(3) Å found in Yb@C\textsubscript{2v}(9)-C\textsubscript{82}/Ni\textsuperscript{II}(OEP), 2.78(2) Å in La@C\textsubscript{2v}(9)-C\textsubscript{82}/Ni\textsuperscript{II}(OEP), and 2.784(8) Å in Gd@C\textsubscript{2v}(9)-C\textsubscript{82}/Ni\textsuperscript{II}(OEP), reflecting the similar interactions between trivalent or divalent M@C\textsubscript{2v}(9)-C\textsubscript{82} and the Ni\textsuperscript{II}(OEP) moiety.

Inside the cage of C\textsubscript{2v}(9)-C\textsubscript{82}, multiple Sm sites were detected. Particularly, three sites (Sm4, Sm5, Sm6) reside on the crystallographic mirror plane, and other sites (Sm1, Sm2, Sm3, Sm7) are on general positions. Among them, Sm1 site has the highest occupancy, while other sites have occupancies ranging from 0.104 to 0.033. Moreover, additional Sm sites (Sm1A, Sm2A, Sm3A, Sm7A) are generated via the crystallographic mirror plane. Thus, there are totally 11 Sm sites inside the disordered C\textsubscript{2v}(9)-C\textsubscript{82} cages. Figure 3 shows the major cage orientation with all these metal sites. Because of the inherent disordered positions of the metal ions combined with a crystallographic mirror plane being mismatched with the
molecular symmetry, the crystallographic data alone cannot determine the assignment of these Sm sites to each cage orientation. Nevertheless, theoretical calculations might provide more useful information. The previously calculated electrostatic potential map of \( [C_9(9)C_{82}]^{12-} \) has demonstrated that the potential minimum is under a hexagon along the \( C_2 \) axis of the \( C_9(9)C_{82} \) cage, which usually corresponds to the position of endohedral divalent metal ion\(^{11b,c} \) (see Figure S3). When considering the major cage orientation of \( C_9(9)C_{82} \), metal sites Sm1–3 and Sm7 are found to be located close to or around the calculated potential minimum, indicating that these sites might be related to the major cage. Among them, the minor site Sm7 resides more closely to the potential minimum as compared to Sm1 and other Sm sites (see Figures S3, S4 for a detailed description). Therefore, DFT optimizations of Sm@\( C_9(9)C_{82} \) were performed at the M06-2X/3-21G \( \sim \) SDD level starting from the models with Sm1 and Sm7 sites, respectively, both of which pointed to a structure as shown in Figure S5. It can be concluded that in the optimized Sm@\( C_9(9)C_{82} \), the Sm\(^{2+} \) ion is located slightly off the \( C_2 \) cage axis with a Sm-hexagon distance of 2.237 Å. It is noteworthy that the optimized Sm\(^{2+} \) position is different from the Sm1 site but very close to the Sm7 site as well as the Yb\(^{2+} \) position in the optimized Yb@\( C_9(9)C_{82} \).\(^{11b} \) The arrangement with the Sm\(^{2+} \) ion right along the \( C_2 \) axis is higher in energy by 0.732 kcal/mol with respect to the optimized Sm@\( C_9(9)C_{82} \). Interestingly, the M06-2X/6-31G\(^* \) \( \sim \) SDD single-point calculations in the observed Sm@\( C_9(9)C_{82}/Ni\( ^{3+}\)(OEP) \) geometries (i.e., without any geometry optimizations, see Figure S4) place the moiety with the Sm7 site by 18.15 kcal/mol higher than the Sm1 species. To this end, despite the occupancy mismatch, it can be seen that the theoretical result, to some extent, agrees with the X-ray result. Therefore, the combined study of X-ray analysis and theoretical calculations might suggest that the preferred position of the Sm\(^{2+} \) ion in Sm@\( C_9(9)C_{82} \) is located slightly off the \( C_2 \) axis of \( C_9(9)C_{82} \). Incidentally, the computed Mulliken charge on Sm is \(+1.955\) e\(^{-}\) confirming the electronic structure of Sm\(^{2+}@[C_9(9)C_{82}]^{12-}\).

As for another Sm@\( C_{82} \) isomer, both the proton decoupled and proton coupled \( ^{13}C \) NMR spectra are shown in Figure 4. Each spectrum displays 16 signals (12 with full intensity, three with half and one with \( 1/6 \)) in the range of 170–110 ppm at 293 K. This pattern can be unambiguously assigned to the cage of \( C_{82}(7)C_{82} \) rather than \( C_{82}(8)C_{82} \). Such a result is consistent with the assignment based on the UV−vis−NIR spectroscopic studies.\(^{12} \) As compared with the previously reported NMR data of Ca@\( C_{82}(7)C_{82} \)\(^{12b} \) which demonstrate signals in the range of 150–130 ppm, the wider signal distribution of Sm@\( C_{82}(7)C_{82} \) again indicates the paramagnetic effect of the endohedral Sm\(^{2+} \) ion. Moreover, because there is only one \( ^{13}C \) NMR signal having \( 1/6 \) intensity in the spectrum, it can be safely assigned to the carbon C(82) (see Figure S6) that is the only carbon residing along the \( C_2 \) axis of the \( C_{82}(7)C_{82} \) cage. Note that this carbon has a lower chemical shift (i.e., 114.96 ppm) relative to most others in the spectrum, indicating a significant paramagnetic effect imposed by the closely located paramagnetic Sm\(^{2+} \) ion. A similar situation was also observed in the \( ^{13}C \) NMR spectrum of \( [Ce@C_{9}(9)C_{82}]^{12-} \), in which the signals with lower chemical shifts were assigned to the hexagon that is along the \( C_2 \) axis and close to the paramagnetic Ce\(^{3+} \) ion. Therefore, the NMR study of Sm@\( C_{82}(7)C_{82} \) might indicate that the internal...
Sm\(^{2+}\) ion prefers to reside along the C\(_3\) axis and very close to the carbon C(82). Such a proposal agrees very well with the previously reported XRD data, which demonstrated a similar Sm\(^{2+}\) ion position as well as a close metal-cage contact between Sm and C(82) in Sm@C\(_{82}\) in Sm@C\(_{82}\)-C\(_{82}\), respectively. A combined study of single crystal X-ray analysis and theoretical calculations suggest that the preferred Sm\(^{2+}\) ion position in Sm@C\(_{82}\)-C\(_{82}\) might be almost negligible. Such a feature suggests that the LUMO+1 orbitals of Sm@C\(_{82}\) isomers are less susceptible to the cage symmetries as compared to their nondegenerate low-lying LUMOs. On the other hand, in the anodic region, the CV of Sm@C\(_{82}\)(7)-C\(_{82}\) at a scan rate of 100 mV s\(^{-1}\) shows an irreversible one-electron oxidation step with a peak potential at 0.66 V. Decreasing the scan rate from 100 mV s\(^{-1}\) to 20 mV s\(^{-1}\), the first oxidation of Sm@C\(_{82}\)(7)-C\(_{82}\) becomes even more irreversible (see Figure S7). The other two isomers both exhibit fully reversible oxidations at 0.52 and 0.42 V (E\(_1/2\) vs Fe/Fe\(^{3+}\)), respectively. Thus, the oxidative behaviors of Sm@C\(_{82}\) isomers are cage-dependent. All these redox steps can also be observed in the corresponding DPV profiles. The electrochemical gap was determined as 1.5 eV for Sm@C\(_{82}\)(7)-C\(_{82}\), 0.94 eV for Sm@C\(_{82}\)(9)-C\(_{82}\), and 1.26 eV for Sm@C\(_{82}\)(5)-C\(_{82}\), respectively, which are consistent with the magnitude of their absorption onset positions (see Table 1). Moreover, another comparison study demonstrated an unremarkable potential difference (less than 90 mV) between Sm@C\(_{82}\)(9)-C\(_{82}\) and Yb@C\(_{82}\)(9)-C\(_{82}\). Also, the potential difference between Sm@C\(_{82}\)(5)-C\(_{82}\) and Yb@C\(_{82}\)(5)-C\(_{82}\) is even smaller than 40 mV.\(^{15}\) These results suggest that replacing the endohedral Yb\(^{2+}\) ion with the Sm\(^{2+}\) ion does not significantly influence the redox properties of M@C\(_{82}\).

### CONCLUSIONS

In conclusion, two Sm@C\(_{82}\) isomers have been structurally characterized by \(^{13}C\) NMR spectroscopy for the first time, and their cage symmetries were unambiguously determined as C\(_{82}\)(9) and C\(_{82}\)(7), respectively. A combined study of single crystal X-ray analysis and theoretical calculations suggest that the preferred Sm\(^{2+}\) ion position in Sm@C\(_{82}\)(9)-C\(_{82}\) might be

| Table 1. Redox Potentials (V vs Fe\(^{0/+}\))\(^{a}\) of Sm@C\(_{82}\)(9)-C\(_{82}\), Sm@C\(_{82}\)(7)-C\(_{82}\), and Reference Fullerenes
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<tr>
<td>Sm@C(<em>{82})(9)-C(</em>{82})</td>
<td>0.52</td>
<td>−0.42</td>
<td>−0.77</td>
<td>−1.60</td>
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<tr>
<td>Yb@C(<em>{82})(9)-C(</em>{82})</td>
<td>0.61</td>
<td>−0.46</td>
<td>−0.78</td>
<td>−1.60</td>
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<tr>
<td>Sm@C(<em>{82})(5)-C(</em>{82})</td>
<td>0.42</td>
<td>−0.84</td>
<td>−1.01</td>
<td>−1.51</td>
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<tr>
<td>Yb@C(<em>{82})(5)-C(</em>{82})</td>
<td>0.38</td>
<td>−0.86</td>
<td>−0.98</td>
<td>−1.50</td>
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<tr>
<td>Sm@C(<em>{82})(7)-C(</em>{82})</td>
<td>0.66 (0.56)</td>
<td>−0.94</td>
<td>−1.25</td>
<td>−1.79</td>
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\(^{a}\)Half-wave potentials unless otherwise noted. \(^{b}\)Irreversible process; peak potential. \(^{c}\)DPV value. \(^{d}\)Ref 11a. \(^{e}\)Ref 16. \(^{f}\)Absorption onset position; units: nm (eV). \(^{g}\)Values reported by ref 13.

Figure 5. Cyclic voltammograms and differential pulse voltammogram of Sm@C\(_{82}\)(9)-C\(_{82}\) (left) and Sm@C\(_{82}\)(7)-C\(_{82}\) (right) in o-dichlorobenzene containing 0.05 M (n-Bu\(_4\))\(_4\)NPF\(_6\) (scan rate: 100 mV s\(^{-1}\) and 20 mV s\(^{-1}\) for CV and DPV, respectively). The asterisk (\(^{*}\)) corresponds to the trace impurities in the sample or solvent.
located in a region slightly off the C$_2$ axis of C$_{60}$. Moreover, the electrochemical surveys on these Sm@C$_{60}$ isomers reveal that their redox activities are mainly determined by the properties of their carbon cages. Therefore, our results not only further complete the knowledge of divalent Mg@C$_{60}$ but also enhance the understanding of the structures and electrochemical properties of these Sm@C$_{60}$ isomers.

### EXPERIMENTAL SECTION

**Synthesis and Isolation.** The synthesis of Sm-metallofullerenes was described in earlier studies. Briefly, Sm-metallofullerenes were produced using a modified arc-discharge method. Specifically, the anode graphite rod was filled with SmNile/graphite powder (1:10 atomic ratio), while a pure graphite rod was employed as a cathode. The arc-discharge was carried out at 70 A with an electrode gap of ca. 1 cm under 400 Torr helium static atmosphere. Fullerene species was extracted from soot using o-xylene at a high temperature under a nitrogen atmosphere. The pure samples of Sm@C$_{60}$ and Sm@C$_{70}$/C$_{60}$ were isolated via a multistage HPLC procedure and then checked by analysis HPLC.

**NMR Experiments.** The $^{13}$C NMR measurements were conducted with a spectrometer (Avance 500 with a Cryo-Probe system; Bruker) in proton-decoupled and proton-coupled modes, respectively. Carbon disulfide was used as a solvent and a capillary tube of acetone-d$_6$ as an internal lock. $^{13}$C NMR (125 MHz, CS$_2$, 293 K) of Sm@C$_{60}$: δ 188.87(2C), 177.56(4C), 162.26(4C), 157.96(4C), 153.65(2C), 152.06(4C), 145.97(4C), 145.85(2C), 145.83(2C), 145.75(4C), 144.78(4C), 144.08(4C), 143.61(4C), 142.00(4C), 141.65(4C), 140.78(4C), 140.21(4C), 139.92(4C), 138.98(6C), 134.68(6C), 134.01(6C), 114.96(1C), 112.62(3C) ppm. $^{13}$C NMR (125 MHz, CS$_2$, 293 K) of Sm@C$_{70}$/C$_{60}$: δ 186.58(3C), 164.03(6C), 159.58(6C), 159.14(6C), 158.61(6C), 153.46(3C), 146.17(6C), 144.87(6C), 143.62(6C), 141.46(6C), 140.69(6C), 139.00(6C), 138.98(6C), 134.68(6C), 134.01(6C), 114.96(1C), 112.62(3C) ppm.

**Single-crystal X-ray Diffraction Analysis.** Black cocrystals of Sm@C$_{60}$-Ni$^{3+}$(OEP) were obtained by allowing the benzene solution of fullerene and the chloroform solution of Ni$^{3+}$(OEP) to diffuse together. X-ray data were collected at 90 K using a diffractometer (APEX II; Bruker Analytik GmbH) equipped with a CCD collector. The multiscan method was used for absorption correction. The structure was resolved using direct methods (SHELX97) and refined on F$^2$ using full-matrix least-squares using SQUEEZE program, a part of the PLATON package of crystallographic analysis. The SQUEEZE analysis was used as a solvent and a capillary tube of acetone-d$_6$ as an internal lock. The SQUEEZE program, a part of the PLATON package of crystallographic analysis, was used. The valence electron density distribution of the SmNi$_2$/C$_{60}$ molecules was modeled using the Gaussian 09 program package at the M06-2X(SDD) level. The standard 3-21G or 6-31G* basis set was used for the C, N, and H atoms and the SDD basis set (with the SDD effective core potential) for Sm and Ni atoms.

### COMPUTATIONAL METHOD

Single point calculations and geometry optimizations were carried out using the Gaussian 09 program package$^{20}$ at the M06-2X/3-21G(6-31G*). The standard 3-21G or 6-31G* basis set was

### TECHNOLOGICAL INNOVATION

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### REFERENCES

Crystal data for Sm@C_{2v}(9)-C_{82}·NiII(OEP)·0.87C_{6}H_{6}·0.13CHCl_{3}: C_{123.34}H_{49.34}Cl_{0.40}SmN_{4}Ni, Mr = 1810.69, 0.28 × 0.15 × 0.12 mm, monoclinic, C2/m (no. 12), a = 25.3280(18), b = 15.1696(11), c = 19.7982(14), β = 95.052(1)°, V = 7577.2(9) Å³, Z = 4, μ (Mo Kα) = 1.097 mm⁻¹, θ = 4.26°–29.57°, T = 90 K, R₁ = 0.1278, wR₂ = 0.3966 for all data; R₁ = 0.1177, wR₂ = 0.3804 for 10 957 reflections (I > 2σ(I)) with 1283 parameters. Maximum residual electron density 1.951 e Å⁻³.


(17) Calculated from DPV values.


