Access to an Unexplored Chiral C_{82} Cage by Encaging a Divalent Metal: Structural Elucidation and Electrochemical Studies of Sm@C_{2(5)}-C_{82}

Wei Xu,[a] Ben Niu,[a, c] Lai Feng,*[b] Zujin Shi,*[a] and Yongfu Lian*[c]

Metal-filled fullerene cages are known as endohedral metallofullerenes (EMFs) that present a unique combination of carbon frame and metallic species at the molecular level. Thus, such species have been considered among the most amazing carbon–metal hybrids.[1] To date, a lot of research has been devoted to revealing their structural features and to the understanding of their chemical and electrochemical properties.[3] Also, studies concerning the potential applications of EMFs in the fields of electronics,[5] photovoltaics or photosynthesis,[6] biomedical,[7] and materials science are currently underway.[8]

M@C_{82} is one of the most abundantly produced EMFs. It has been proved that the endohedral metal M might be either trivalent (e.g., M = La, Ce, Gd, Y)[7] or divalent (e.g., M = Yb, Sm, Eu).[8] Accordingly, the cage of M@C_{82} is either 3-fold or 2-fold negatively charged because of the electron-transfer from the metal to the cage. Recently, to further inspect the metal–cage interplay, many of studies focused on the structures and relative stabilities of these differently charged C_{82} cages. For instance, it has been revealed that the cages of C_{2v}-C_{82} and C_{s}(6)-C_{82} can be highly stabilized by encaging a trivalent metal.[9,10] However, as for divalent M@C_{82} such as Yb@C_{82}, totally four isomeric C_{82} cages have been detected.[8b] Through a combined study of NMR spectroscopy and DFT-calculations, three of them were determined as C_{2(5)}-C_{82}, C_{s}(6)-C_{82}, and C_{2v}-C_{82}, respectively. Among these cages, C_{2(5)}-C_{82} is more distinctive, because it is only available for divalent M@C_{82} and has never been found for trivalent M@C_{82} or for empty C_{82} fullerenes. It appears that the formation of C_{2(5)}-C_{82} cage is only achieved by encaging a divalent metal (i.e., Sm), suggesting that the cage of C_{2(5)}-C_{82} with a trivalent metal or without any endohedral species inside does not have sufficient stability. Also, C_{2(5)}-C_{82} is a chiral cage and has never been experimentally observed.[10]

Herein, we report a new chiral metallofullerene Sm@C_{2(5)}-C_{82}, its structural characterizations, and electrochemical studies. Particularly, the chiral C_{2(5)}-C_{82} cage and the motional Sm atom have been unambiguously identified using crystallographic methods. In addition, the featured oxidative properties of Sm@C_{2(5)}-C_{82} are clearly presented.

The sample of Sm@C_{2(5)}-C_{82} was produced and isolated according to a previously reported procedure.[8b] The absolute structure of Sm@C_{2(5)}-C_{82} was determined using single-crystal X-ray diffraction (XRD). Co-crystals of Sm@C_{2(5)}-C_{82}/[Ni^{II}OEP] suitable for X-ray analysis were obtained by slow diffusion of a benzene solution of Sm@C_{2(5)}-C_{82} into a CHCl_{3} solution of [Ni^{II}OEP]. The molecular structure was resolved and refined with a monoclinic C_{2} space group. Figure 1 shows the X-ray structure of Sm@C_{2(5)}-C_{82} together with an adjacent [Ni^{II}OEP] moiety, in which the fully ordered C_{2(5)}-C_{82} cage is clearly identi-
fied. Because of the high symmetric space group, another cage with symmetry-related orientation can be generated through a crystallographic mirror plane. Notable are the different chiral elements presented by these two $C_2(5)$-$C_{82}$ cages. As shown in Figure 2, the three dimensional diagrams of these two $C_2(5)$-$C_{82}$ cages are depicted with enantiomeric systematic numbering schemes. It is clear that they are enantiomeric species, having a $^{13}$C configuration with clockwise helixe and a $^{13}$A configuration with anticlockwise helixe, respectively. Thus, this cocrystal contains racemic Sm$@C_2(5)$-$C_{82}$ with a pair of enantiomers in 1:1 ratio.

Inside the $C_2(5)$-$C_{82}$ cage, eight partially occupied Sm sites have been identified (Figure 3). The major Sm site (i.e., Sm1) with a fractional occupancy of 0.174 is apart from the $C_2$ axis and is suited under a hexagonal ring with a centroid-to-metal distance of 2.258 Å, while the shortest cage carbon-to-metal distance is 2.498 Å. Such alignment is common in EMFs and might suggest a preferred to-metal distance is 2.498 Å. Such alignment is common in EMFs and might suggest a preferred to-metal distance is 2.498 Å, while the shortest cage carbon-

![Figure 2](image2.png)

Figure 2. Three-dimensional diagrams of two symmetry-related $C_2(5)$-$C_{82}$ cages with enantiomeric (left and right) systematic numbering schemes, showing their $^{13}$C and $^{13}$A configurations, respectively.

Furthermore, Sm$@C_2(5)$-$C_{82}$ was characterized by $^{13}$C NMR studies. When using CS$_2$ as solvent, 40 signals with equal intensity were observed in the 190–80 ppm region in either proton-decoupled or proton-coupled $^{13}$C NMR spectrum (Figure 4). On closer inspection, another $^{13}$C signal broader than those 40 signals, was detected at 206.90 ppm, and might be also assigned to the cage carbons. Thus, the presence of totally 41 $^{13}$C signals corroborate well with the $C_2$-symmetric $C_{82}$ cage, consistent with the X-ray analysis result. When compared with Ca$@C_{82}$(III)[12] and Yb$@C_{82}$(II)[10] which have been proposed having the same cage structure, the $^{13}$C signals of Sm$@C_2(5)$-$C_{82}$ are distributed over a wider range (i.e., 207–80 ppm) and undergo shifts with varied temperature. The presence of six unpaired $f$ electrons on the endohedral Sm atom might account for these features. Specifically, these unpaired electrons can significantly affect the local magnetic field and the fast relaxation of $^{13}$C nuclear spins on the nearby cage carbons.[9b] In addition, further investigation was performed with variable-temperature (VT) $^{13}$C NMR experiments and revealed that the signal at 206.90 ppm underwent larger temperature-dependent shift (i.e., $\Delta \delta = 3$ ppm, from 303 K to 293 K) than all the other signals (see Figure S1 in the Supporting information). Therefore, this most shifted signal might be assigned to the cage carbons nearest to the Sm atom. In comparison, the $^{13}$C signals of Tm$@C_{82}$(II), which also has a $C_2$-symmetric cage, are distributed over even wider range (i.e., 320–0 ppm) because of an unpaired $f$ electron on the Tm atom and probably shorter metal–cage distance relative to that of Sm$@C_2(5)$-$C_{82}$.

![Figure 3](image3.png)

Figure 3. Drawing of Sm$@C_2(5)$-$C_{82}$, showing the locations of the various partially occupied Sm sites inside the cage. These Sm sites labeled “A” are generated through the crystallographic mirror plane. Occupancies of Sm sites are as following: Sm1 0.174(4), Sm2 0.111(10), Sm3 0.087(11), Sm4 0.023(4), Sm5 0.049(4), Sm6 0.039(6), Sm7 0.0063 (18) and Sm8, 0.0076 (17).

The electrochemical properties of Sm$@C_2(5)$-$C_{82}$ were studied by means of cyclic voltammogram (CV) and differential pulse voltammogram (DPV), as shown in Figure 5. S2 and S3. CV and DPV were recorded in $o$-dichlorobenzene ($o$-DCB) rather than toluene/acetonitrile used in the previ-
ous report.[8b] Tetra-(n-butyl)-ammoniumhexafluorophosphate (nBu4NPF6; 0.05 m) was used as supporting electrolyte. Under such conditions, an one-electron oxidation process can be observed at 0.42 V (E1/2), which is 40 mV higher than that of Yb@C60(II).[18] Notable is that such oxidation process is otherwise invisible in the toluene/acetonitrile system previously described.[8b] Besides, CV measurements suggest that the oxidation of Sm@C70(5-C82) is quasi-reversible. When increasing the scan rate from 100 mVs⁻¹ to 800 mVs⁻¹, this oxidation process becomes more reversible (see Figure S2 in the Supporting Information). In contrast, the one-electron oxidation of Yb@C60(II) is fully reversible.[18] Consequently, it appears that the changes in the ionic radii of endohedral metals can influence the oxidative behavior of divalent M@C60, whereas such trend is less remarkable for trivalent M@C60.[21] In the cathodic side, four one-electron reductions appeared at −0.84 (E1/2), −1.01 (E1/2), −1.51 (E1/2), and −1.90 V (E1/2), respectively, all showing perfect reversibility. These reduction potentials are very close to those of Yb@C60(II). In addition, the electrochemical potential gap of Sm@C70(5-C82) is determined as 1.29 V.

In conclusion, we have unambiguously characterized a new chiral metallofullerene Sm@C70(5-C82), including its cage structure, and the unprecedented motional behavior of the endohedral Sm atom. In the 13C NMR spectra, a total of 41 signals were observed in the 210–80 ppm region, thus corroborating the results obtained upon X-ray analysis. In addition, a quasi-reversible oxidation process of Sm@C70(5-C82) was identified for the first time, which is different from that of Yb@C60(II), and indicates a metal-induced effect on the redox properties of divalent M@C60.

Experimental Section

The sample of Sm@C70(5-C82) was produced by evaporation of graphite via the direct current arc discharge method, details of which have been published elsewhere.[19] Black co-crystals of Sm@C70(5-C82)-Ni(OEP) were obtained by allowing the benzene solution of the fullerenes and the chloroform solution of Ni(OEP) to diffuse together. X-ray data were collected at 90 K using a diffractometer (APEX-II; Bruker Analytik GmbH) equipped with a CCD detector. Numerical methods were used for absorption correction. The structures were resolved using direct methods (SHELXS97) and refined on F² using full-matrix least squares using SHELXL97.[20] In refinement, the intact cage was modeled via the crystallographic mirror plane. The sum of the occupancy factors for all Sm sites was set as 0.5, while the cage occupancy is 0.5. Hydrogen atoms were added geometrically and refined with a riding model. Co-crystals of Sm@C70(5-C82)-Ni(OEP) were not able to be modeled properly. Therefore, program SQUEEZE, a part of the PLATON package of crystallographic software,[20] was used to calculate the solvent disorder area and remove its contribution from the intensity data.

Crystal data for Sm@C70(5-C82)-Ni(OEP)·0.57CHCl3·0.43C6H6·C121.15H47.15Cl1.71SmN4Ni, M = 1828.26, 0.25 × 0.15 × 0.15 mm, monoclinic, C2/m, a = 25.2864(19), b = 15.1163(10), c = 19.7557(14), β = 94.04084(7), V = 7526.0(9) Å³, Z = 4, µ(Mo Kα) = 1.614 g/cm³, µ(Mo Kα) = 1.150 mm⁻¹, θ = 1.57–27.10°, θ = 90 K, R1 = 0.0887, wR2 = 0.2046 for all data; R1 = 0.0726, wR2 = 0.1933 for 6681 reflections (I > 2σ(I)) with 1022 parameters. Maximum residual electron density 0.781 eÅ⁻³.

More detailed crystal data are presented in Table S1 in the Supporting Information. CCDC-2155347 (Sm@C70(5-C82)-Ni(OEP)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The 13C NMR measurements were conducted on a spectrometer (Avance 500 with a Cryo-Probe system; Bruker) in carbon disulfide using a capillary tube of [D₆]acetone as internal lock. 13C NMR (125 MHz, CS₂, 293 K): δ = 206.89, 184.72, 181.30, 178.04, 165.53, 164.74, 159.66, 156.21, 155.56, 155.41, 151.42, 150.89, 150.58, 149.46, 148.78, 148.16, 147.43, 146.11, 145.42, 144.74, 143.99, 143.68, 143.24, 142.24 (overlapped), 141.32, 141.21, 141.06, 140.94, 140.36, 136.45, 135.85, 135.61, 135.03, 131.59, 131.07, 126.13, 120.76, 103.65, 80.33 ppm. The VT 13C NMR spectra (see the Supporting Information) were recorded in o-[D₆]DCB at 303 K, 293 K, and 283 K, respectively.

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were carried out in o-DCE using a BAS CW-50 instrument. A conventional three-electrode cell consisting of a platinum working electrode, a platinum counter-electrode, and a saturated calomel reference electrode. All potentials were recorded against a SCE reference electrode and corrected against FeC/Fè. DPV and CV were measured at a scan rate of 20 and 100 mVs⁻¹, respectively.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (No. 21171013, 51072047), the Ministry of Science and Technology of China (No. 2013CB933402, 2011CB932601), and the NSFC of the Jiangsu province of China (No. BK2012611). Also, we are grateful to prof. T. Akasaka, Dr. Z. Slanna, and Dr. M. Suzuki at University of Tsukuba for their helpful discussions and XRD measurement.

Keywords: electrochemistry · fullerenes · NMR spectroscopy · structure elucidation · X-ray diffraction