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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.^[2] Also, studies concerning the potential applications of EMFs in the fields of electronics,^[3] photovoltaics or photosynthesis,^[4] biomedicine,^[5] and materials science are currently underway.^[6]

$M@C_{82}$ 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.^[7c,9] However, as for divalent $M@C_{82}$ such as $Yb@C_{82}$, totally four isomeric C_{82} cages have been detected.^[8a] 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 $C2m$ 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-

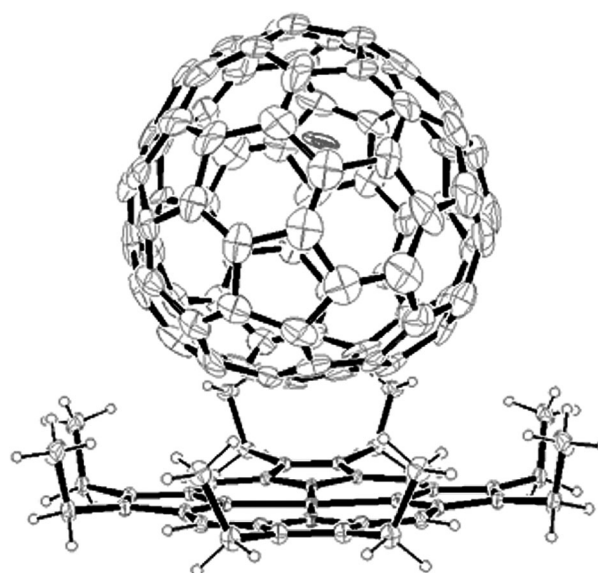


Figure 1. Ortep drawing of $Sm@C_2(5)-C_{82}\cdot Ni^{II}(OEP)$ with 25% thermal ellipsoids, showing the intermolecular interaction. The major Sm site with fractional occupancy of 0.174 is depicted. Solvent molecules are omitted for clarity.

[a] Dr. W. Xu, B. Niu, Prof. Dr. Z. Shi
Beijing National Laboratory for Molecular Sciences
State Key Lab of Rare Earth Materials Chemistry and Applications
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871 (P.R. China)
Fax: (+86)10-62751708
E-mail: zjshi@pku.edu.cn

[b] Prof. Dr. L. Feng
Jiangsu Key Laboratory of Thin Films and School of Energy
Soochow University
Suzhou 215006 (P.R. China)
E-mail: fenglai@suda.edu.cn

[c] B. Niu, Prof. Y. Lian
School of Chemistry and Materials Science
Heilongjiang University,
Harbin 150081 (P.R. China)
E-mail: chyflian@hlju.edu.cn

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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 ${}^{f,s}C$ configuration with clockwise helice and a ${}^{f,s}A$ configuration with anticlockwise helice, respectively. Thus, this cocrystal contains racemic $Sm@C_2(5)-C_{82}$ with a pair of enantiomers in 1:1 ratio.

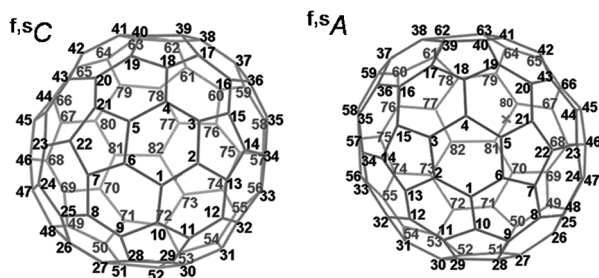


Figure 2. Three-dimensional diagrams of two symmetry-related $C_2(5)-C_{82}$ cages with enantiomeric (left and right) systematic numbering schemes, showing their ${}^{f,s}C$ and ${}^{f,s}A$ configurations, respectively.

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 η^6 metal-cage contact. Other Sm sites with fractional occupancies ranging from 0.111 to 0.006 are distributed randomly inside cage, suggesting a motional behavior of endohedral Sm atom inside the cage of $C_2(5)-C_{82}$ even at 90 K. This result is unlike the previously reported $M@C_{2v}-C_{82}$ ($M=La, Ce, Gd$),^[11] in which the trivalent metal atom is highly localized under a hexago-

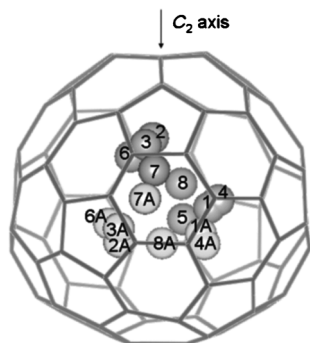


Figure 3. Drawing of $Sm@C_2(5)-C_{82}$, showing the locations of the various partially occupied Sm sites inside the cage. These Sm sites labeled "A" are generated through the crystallographic mirror plane. Occupancies of Sm sites are as following: Sm1 0.174(4), Sm2 0.111(10), Sm3 0.087(11), Sm4 0.023(4),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

nal ring and along the C_2 axis of the cage. It appears that the motional behavior of endohedral metal is highly dependent on the cage structure as well as the metal-cage interaction.

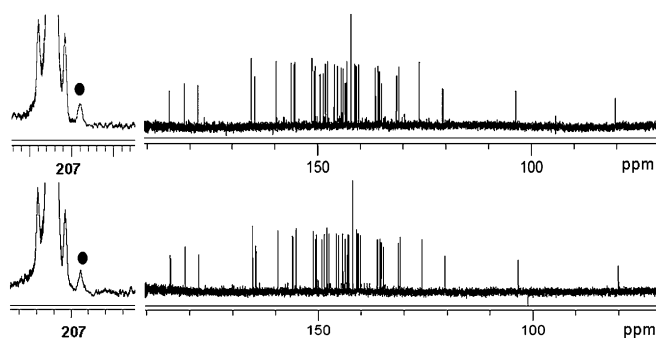


Figure 4. ${}^{13}C$ NMR spectra (125 MHz, in CS_2 using $[D_6]acetone$ as internal lock) of $Sm@C_2(5)-C_{82}$, measured at room temperature in proton-decoupled (top) and proton-coupled (bottom) mode, respectively. ● indicates a ${}^{13}C$ signal of cage carbon at lower field.

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 $Yb@C_{82}(II)$,^[8a] 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.^[9a] 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 $Sm@C_2(5)-C_{82}$.^[8e]

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-

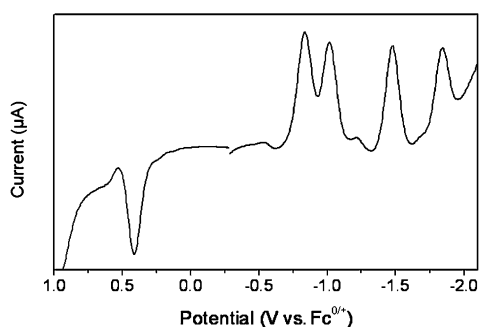


Figure 5. Differential pulse voltammogram of Sm@C₂(5)-C₈₂ in *o*-dichlorobenzene (0.05 M (nBu)₄NPF₆, 20 mVs⁻¹ scan rate).

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 (^{ox}E₁), which is 40 mV higher than that of Yb@C₈₂(II).^[8a] 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@C₂(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@C₈₂(II) is fully reversible.^[8a] Consequently, it appears that the changes in the ionic radii of endohedral metals can influence the oxidative behavior of divalent M@C₈₂, whereas such trend is less remarkable for trivalent M@C₈₂.^[2a] In the cathodic side, four one-electron reductions appeared at -0.84 (^{red}E₁), -1.01 (^{red}E₂), -1.51 (^{red}E₃), and -1.90 V (^{red}E₄), respectively, all showing perfect reversibility. These reduction potentials are very close to those of Yb@C₈₂(II). In addition, the electrochemical potential gap of Sm@C₂(5)-C₈₂ is determined as 1.29 V.

In conclusion, we have unambiguously characterized a new chiral metallofullerene Sm@C₂(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@C₂(5)-C₈₂ was identified for the first time, which is different from that of Yb@C₈₂(II), and indicates a metal-induced effect on the redox properties of divalent M@C₈₂.

Experimental Section

The sample of Sm@C₂(5)-C₈₂ was produced by evaporation of graphite via the direct current arc discharge method, details of which have been published elsewhere.^[8b] Black co-crystals of Sm@C₂(5)-C₈₂Ni^{II}(OEP) were obtained by allowing the benzene solution of the fullerene and the chloroform solution of Ni^{II}(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. 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.^[13] 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@C₂(5)-C₈₂Ni^{II}(OEP)-0.57CHCl₃-0.43C₆H₆ contains another severely disordered lattice of C₆H₆ and CHCl₃ molecules that could not be modeled properly. Therefore, program SQUEEZE, a part of the PLATON package of crystallographic software,^[14] was used to calculate the solvent disorder area and remove its contribution from the intensity data.

Crystal data for Sm@C₂(5)-C₈₂Ni^{II}(OEP)-0.57CHCl₃-0.43C₆H₆: C_{121.15}H_{47.15}Cl_{1.71}SmNi₂Ni, M_r = 1828.26, 0.25 × 0.18 × 0.15 mm, monoclinic, C2m, a = 25.2864(19), b = 15.1103(10), c = 19.7557(14), β = 94.408(4)°, V = 7526.0(9) Å³, Z = 4, ρ_{calcd} = 1.614 g cm⁻³, μ(MoKα) = 1.150 mm⁻¹, θ = 1.57–27.10°, T = 90 K, R₁ = 0.0887, wR₂ = 0.2046 for all data; R₁ = 0.0726, wR₂ = 0.1933 for 6681 reflections (I > 2.0σ(I)) with 1022 parameters. Maximum residual electron density 0.781 e Å⁻³.

More detailed crystal data are presented in Table S1 in the Supporting Information. CCDC-2155347 (Sm@C₂(5)-C₈₂Ni^{II}(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, 165.51, 164.74, 159.66, 156.21, 155.56, 155.41, 151.42, 150.89, 150.58, 149.46, 148.74, 148.16, 147.43, 146.11, 145.42, 144.47, 143.99, 143.48, 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, 80.03 ppm. The VT ¹³C NMR spectra (see the Supporting information) were recorded in *o*-[D₄]DCB at 303 K, 293 K, and 283 K, respectively.

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were carried out in *o*-DCB 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 (SCE) was used for both measurements. 0.05 M (nBu)₄NPF₆ was used as the supporting electrolyte. All potentials were recorded against a SCE reference electrode and corrected against Fc/Fc⁺. DPV and CV were measured at a scan rate of 20 and 100 mVs⁻¹, respectively.

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

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