Beyond the Butterfly: Sc$_2$C$_2$@C$_{2v}$(9)-C$_{86}$, an Endohedral Fullerene Containing a Planar, Twisted Sc$_2$C$_2$ Unit with Remarkable Crystalline Order in an Unprecedented Carbon Cage

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S Supporting Information

ABSTRACT: The synthesis, isolation, and characterization of a new endohedral fullerene, Sc$_2$C$_{88}$, is reported. Characterization by single crystal X-ray diffraction revealed that it is the carbide Sc$_2$C$_2$@C$_{2v}$(9)-C$_{86}$ with a planar, twisted Sc$_2$C$_2$ unit inside a previously unseen C$_{2v}$(9)-C$_{86}$ fullerene cage.

One of the most fascinating properties of fullerenes is their ability to encapsulate atoms, ions, small molecules, or metallic clusters.[1−4] The endohedral fullerene field started with the discovery of La@C$_{82}$ by Smalley et al. in 1985,[5] but it was not until the macroscopic production of fullerenes in 1990 when the study of endohedral fullerene properties and reactivity was possible.[6,7] The first cluster endohedral fullerene was discovered by Stevenson et al. in 1999, with the isolation of the most abundant endohedral fullerene, Sc$_3$N@I$_h$-C$_{80}$.[8] These extensively studied compounds exhibit high stability due to the transfer of multiple electrons from the inner cluster to the carbon cage, leading to what is commonly represented as [Sc$_3$N]$^{6+}$[C$_{80}$]$^{6−}$.[4,7,9] It is well-known that the size, shape, and charge of the encapsulated cluster play important roles in the selection of a complementary carbon cage.[9]

Endohedral fullerenes with M$_2$C$_{2n}$ compositions can exist as conventional endohedrals, M$_2$@C$_{2n}$, or as metal carbide clusters, M$_2$C$_2$@C$_{2n-2}$.[10,11] In 2001, the structure of Sc$_2$C$_{86}$ was unambiguously assigned as the first metal carbide clusterfullerene (MCCF), Sc$_2$C$_2$@D$_{2d}$(23)-C$_{84}$, as opposed to Sc$_2$@C$_{86}$.[12] Interestingly, in all reported cases the M$_2$C$_2$ cluster exhibits what has been described as a butterfly shape, which is illustrated in Scheme 1.[10,11] Molecules of the type M$_2$C$_2$@C$_{2n-2}$ that have been crystallographically characterized include Sc$_2$C$_2$@C$_s$(10528)-C$_{72}$,[13] Sc$_2$C$_2$@C$_{2v}$(5)-C$_{80}$,[14] Sc$_2$C$_2$@C$_{3v}$(8)-C$_{82}$,[14,15] Sc$_2$C$_2$@D$_{2d}$(23)-C$_{84}$,[14] Gd$_2$C$_2$@C$_1$(51383)-C$_{84}$,[16] Gd$_2$C$_2$@D$_3$(85)-C$_{92}$,[17] Tm$_2$C$_2$@C$_s$(6)-C$_{82}$,[18] and Tb$_2$C$_2$@C$_s$(6)-C$_{82}$.[19] Unfortunately, these structures suffer some form of disorder. Generally, there is disorder in the positions of the metal ions, but there can also be disorder in the position of the carbide units. Nevertheless, all these examples have been found to contain the generalized butterfly shape shown in Scheme 1. However, the disorder makes it difficult to specify a single M−M separation or the dihedral angle between the two MC$_2$ planes. In the cases of Gd$_2$C$_2$@C$_1$(51383)C$_{84}$[16] and Gd$_2$C$_2$@D$_3$(85)-C$_{92}$[17] the metal

Scheme 1. Structural Arrangements for M$_2$C$_2$ Units within Fullerenes: Top, Observed Butterfly Shapes; Bottom, Computational Suggestions

Butterfly Shapes

acutely bent   bent   planar
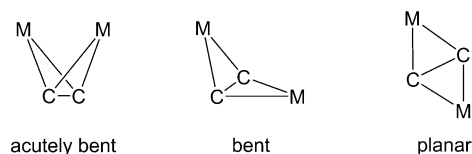
Structural Effects of the Elongation of the Metal-Metal Distance
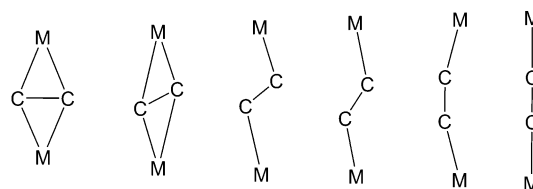
ion positions suggest that the metal ions may be free to move about the C$_2$ unit by executing a wing-flapping motion.

Dorn and co-workers have suggested that fullerene cage sizes may influence the shape of the M$_2$C$_2$ unit in endohedrals containing the M$_2$C$_2$ unit by compressing it.[20] They suggested that as the cage size expands the M$_2$C$_2$ unit could also expand as shown in the lower part of Scheme 1. Eventually, a linear MCCM unit is formed, which is the situation in the acetylide modification of the carbide in calcium carbide.[21] Deng and Popov have also considered the shape of the M$_2$C$_2$ unit in various cage environments and considered alternative structures similar to those shown in Scheme 1.[22] Irle et al. performed a computational study of the geometry of the Sc$_2$C$_2$ unit within Sc$_2$C$_2$@C$_{3v}$-C$_{82}$ and suggested that nonlinear structures might be stable.[23] Here, we present definitive evidence for the existence of a unanticipated, twisted structure of an enclosed M$_2$C$_2$ unit inside an unprecedented C$_{2v}$(9)-C$_{86}$ carbon cage.

Sc$_2$C$_{88}$ was synthesized in a modified Krätschmer−Huffman arc-discharge reactor using a mixture of Sc$_2$O$_3$ and graphite

(molar ratio of Sc/C = 1:15) as the raw material in a 200 mbar helium atmosphere. The crude mixture of empty and scandium endohedral fullerenes was analyzed by high performance liquid chromatography (HPLC) in a 5PYE column using toluene as the mobile phase and a flow rate of 3.00 mL min^{-1}, as shown in Figure SI-1. Only one isomer of Sc_2C_{88} was found. The purity of this sample was confirmed by the final chromatogram and the matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) spectrum shown in Figure 1 (peak at m/z 1145.899). The isotopic distribution of the experimental spectrum matches that theoretically calculated for Sc_2C_{88}, as seen in the inset.
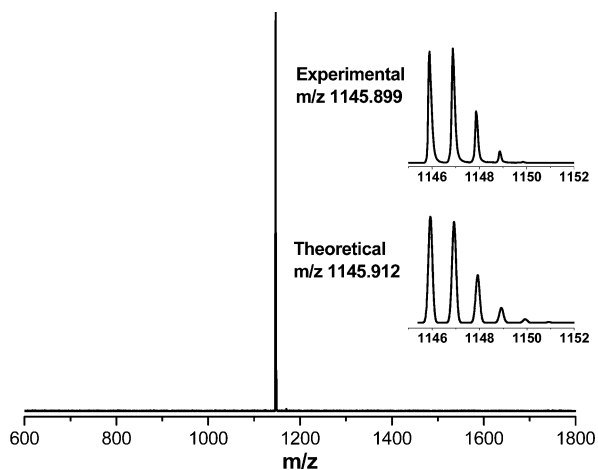
Figure 1. Mass spectrum of the purified Sc_2C_{88}. Inset: Experimental and theoretical isotopic distributions for Sc_2C_{88}.

The vis−NIR absorption of a carbon disulfide solution of Sc_2C_{88} exhibited peaks at λ_{max} = 411, 613, 690, 755, 947, 1081, 1730, 1750 nm as seen in Figure 2. The vis−NIR absorption of
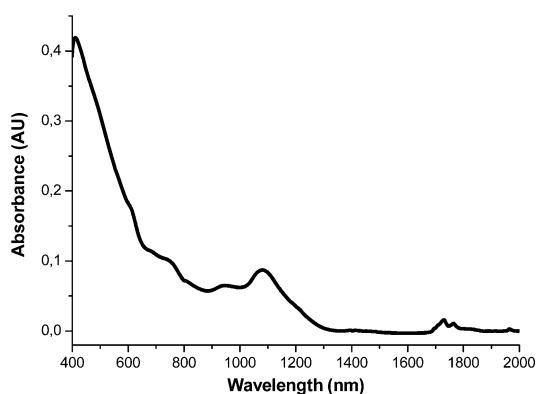

Figure 2. Vis−NIR absorption of Sc_2C_{88} in CS_2 solution.

endohedral fullerenes in the visible and NIR are mostly due to $\pi-\pi^*$ transitions of the fullerene cage, which are determined by the isomeric structure and the charge state of the fullerene cage.[24] The spectrum in Figure 2 is substantially different from the spectra of other crystallographically characterized compounds involving the C_{88} cage: $Sm_2@D_2(35)-C_{88}$,[25] $Gd_2C_2@D_2(35)-C_{88}$,[26] and $Tb_3N@D_2(35)-C_{88}$.[27] The characteristic features of the observed vis−NIR spectrum are also substantially different from those reported for $Tb_3N@D_3(17)-C_{86}$[24] and $Gd_3N@D_3(17)-C_{86}$,[28] which are crystallographically characterized endohedral fullerenes possessing a C_{86} cage. The spectrum is

also different from those of the empty cage isomers, $C_2(17)-C_{86}$ and $C_s(16)-C_{86}$.[29,30] The remarkable differences between the absorption spectrum of Sc_2C_{88} and those of all of the reported C_{86} and C_{88} isomeric cages are consistent with the presence of a different carbon cage symmetry in the present case.

Slow diffusion of toluene solutions containing Sc_2C_{88} and Ni(OEP) (OEP is the dianion of octaethylporphyrin) produced black block crystals of $Sc_2C_2@C_{2v}(9)-C_{86}·Ni(OEP)·2C_7H_8$. The crystals were quite small and suffered severe twinning. The endohedral fullerene was determined to be a carbide with an Sc_2C_2 unit trapped within a fairly symmetrical cage, $C_{2v}(9)-C_{86}$.

Figure 3 shows the fullerene and interior contents with the 2-fold axis of the fullerene aligned vertically. The Sc_2C_2 unit is
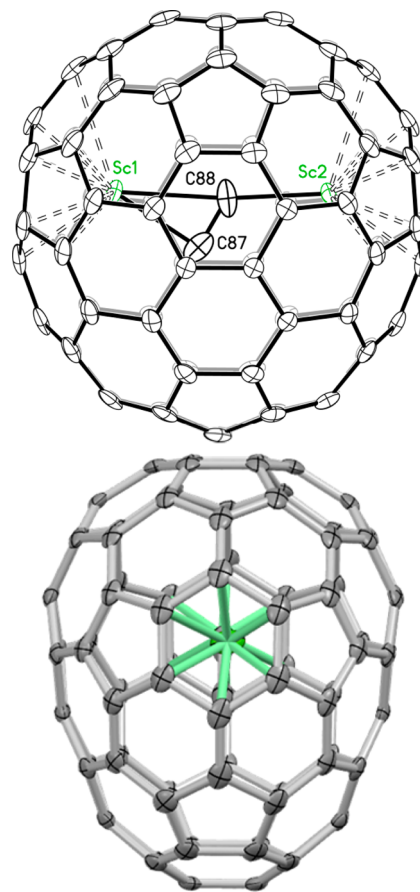
Figure 3. Two orthogonal views of the fullerene component of $Sc_2C_2@C_{2v}(9)-C_{86}·Ni(OEP)·2C_7H_8$ showing key cluster−cage interactions. The thermal contours are drawn at the 50% probability level. Ni(OEP) and toluene molecules are omitted for clarity.

positioned unsymmetrically within this cage so that the entire molecule no longer has C_{2v} symmetry. Within the crystal the molecule shown in Figure 3 is fully ordered, an unusual situation since most endohedral fullerenes even when cocrystallized with Ni(OEP) show some sort of disorder in either the positioning of the metal or metal cluster within the cage, in the cage orientation itself or in both.[31] The only other case of which we are aware that involves a fully ordered endohedral is found in only one of the two molecules of $Sc_2(\mu_2-S)@C_s(6)-C_{82}$ in the asymmetric unit of $Sc_2(\mu_2-S)@C_s(6)-C_{82}·Ni(OEP)·2C_6H_6$.[32]

Figure 4 shows the details of the structure of the Sc_2C_2 unit. The cluster adopts a planar, twisted geometry, which places Sc1 close to both carbide carbon atoms but Sc2 is near only one of
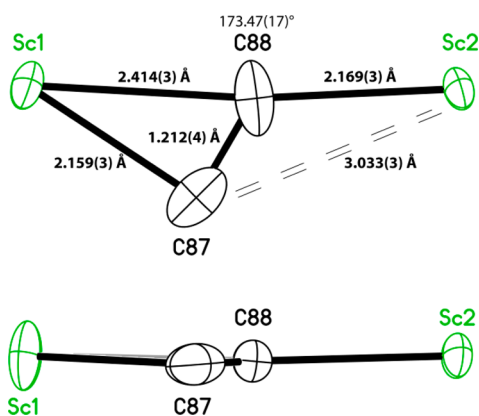
Figure 4. (Top) Interior carbide cluster bonding motif showing the atomic distances. (Bottom) Orthogonal view illustrating the planarity of the cluster. Thermal contours are drawn at the 50% probability level.

these. The distance between Sc atoms inside the cage is 4.5760(6) Å. The carbon−carbon bond length is 1.212(4) Å, which is typical for endohedral fullerene carbides.[10,11] This planar arrangement is unlike any other seen for a metal carbide endohedral fullerene and differs markedly from the structures obtained computationally for the expansion of the metal−metal separation as shown in Scheme 1. However, Irle and co-workers briefly mention a computed structure for $Sc_2C_2@C_{2v}(9)$-C_{86}, which has some similarity to the experimental structure determined here.[23] The scandium ions are symmetrically positioned over hexagonal faces of the carbon cage as seen in the lower drawing in Figure 3. The six shortest Sc···C cage distances are in the range 2.267(2)−2.495(2) Å around Sc1 and 2.272(2)−2.470(2) Å around Sc2. The lower part of Figure 3 also emphasizes the wedge-shaped nature of the $C_{2v}(9)$-C_{86} cage with its flattened sides. The pyramidalization of the cage carbon atoms[33] ranges from 5.58° on the flat sides to as high as 12.82° where the Sc ions are in close proximity to the cage.

The interaction between the $Sc_2C_2@C_{2v}(9)$-C_{86} molecule and the Ni(OEP) molecule is shown in Figure 5. Generally, the metal centers in endohedral fullerenes are found close to the porphyrin
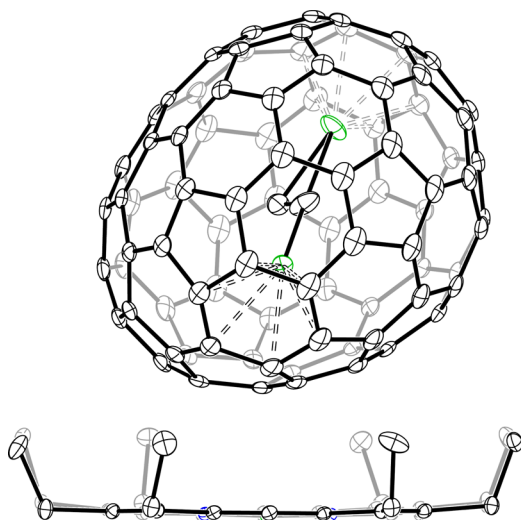

Figure 5. Orientation of the $Sc_2C_2@C_{2v}(9)$-C_{86} molecule relative to the planar Ni(OEP) molecule in $Sc_2C_2@C_{2v}(9)$-C_{86}·Ni(OEP)·2C_7H_8. Thermal contours are drawn at the 50% probability level. Toluene molecules are omitted for clarity.

plane in such cocrystals.[34] However, the geometry of $Sc_2C_2@C_{2v}(9)$-C_{86} allows only one of the scandium ions to be positioned near the planar porphyrin. Although the $C_{2v}(9)$-C_{86} cage possesses two rather flat sides, neither is positioned near the porphyrin. Nevertheless, the crystal is fully ordered with the unsymmetrical location of the internal carbide unit somehow able to communicate its location so that full ordering of the cage takes place.

Due to the considerable disorder in the $Sc_2C_2@C_{2n}$ carbide structures, it is only possible to give approximate estimates of how the geometry of the M_2C_2 unit conforms to the particular cage size and isomer. The variation in separation between the two scandium ions is estimated for the following cages: $Sc_2C_2@C_s(10528)$-C_{72},[13] 4.2 Å; $Sc_2C_2@C_{2v}(5)$-C_{80},[14] 4.31 Å; $Sc_2C_2@C_{3v}(8)$-C_{82}, 3.98 Å;[14,15] $Sc_2C_2@D_{2d}(23)$-C_{84}, 4.46 Å;[14] $Sc_2C_2@C_{2v}(9)$-C_{86}, 4.5760(6) Å. Clearly, the Sc···Sc separation increases as the cage size expands.

The redox potentials of $Sc_2C_2@C_{2v}(9)$-C_{86} were measured by cyclic voltammetry (CV) in an o-dichlorobenzene (o-DCB) solution containing 0.05 M n-Bu$_4$NPF$_6$ as the supporting electrolyte. The CV of results is shown in Figure 6. One is
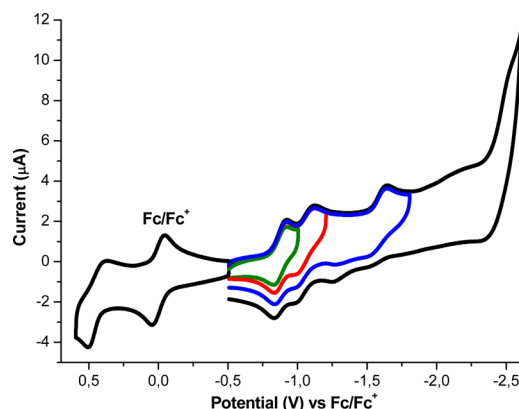
Figure 6. Cyclic voltammogram of $Sc_2C_2@C_{2v}(9)$-C_{86} in 0.05 M n-Bu$_4$NPF$_6$/o-DCB solution.

reversible, and three irreversible reductive processes are observed along with one reversible oxidation, qualitatively similar behavior to that reported for $Sc_2C_2@C_{2v}$-C_{82} (Table 1, Supporting Information).[35] For comparison, $M_3N@C_{86}$ (M = Gd, Nd, and Pr) showed three irreversible reductions and one reversible oxidation processes.[36,37] Thus, changing the symmetry of the cage and the encapsulated cluster significantly affect the redox properties of endohedral fullerene.[7,9] Remarkably, changing the cage size from C_{2v}-C_{82} to C_{2v}-C_{86} mainly affected the oxidation process of $Sc_2C_2@C_{2v}$-C_{86} for which a 220 mV anodic shift was observed.[9,35]

In summary, a new metal carbide clusterfullerene, $Sc_2C_2@C_{2v}(9)$-C_{86} has been synthesized, isolated, and characterized. Importantly, the planar, twisted arrangement of the inner Sc_2C_2 unit has been experimentally observed for the first time. Further computational and experimental studies are clearly needed to address the issue of the unusually twisted structure we have found. The crystallographic ordering of this fullerene may originate in its somewhat unsymmetric shape and its dipolar nature. Interestingly, the empty cage $C_{2v}(9)$-C_{86} has been computed to be the least stable of the 19 isomers of C_{86} that obey the isolated pentagon rule.[38,39] Further investigations that examine the regioselective reactivity of this cage will be of interest

in comparison to the recent studies of the reactivity of $Sc_2C_2@C_s(6)$-C_{82}.[40] and $Sc_2C_2@C_{3v}(8)$-C_{82}.[41]

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06425.

  X-ray crystallographic file (CIF)
  Experimental section, HPLC chromatograms of the purified $Sc_2C_2@C_{2v}(9)$-C_{86}, redox potentials, structural packing diagram, atom numbering scheme, POAV analysis, Strauss plot, and additional cluster geometry (PDF)

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Notes
The authors declare no competing financial interest.

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