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$Sc_2C_2@C_{80}$ Rather than $Sc_2@C_{82}$: Templated Formation of Unexpected $C_{2v}(5)$-C_{80} and Temperature-Dependent Dynamic Motion of Internal Sc_2C_2 Cluster

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S Supporting Information

ABSTRACT: Unambiguous X-ray crystallographic results of the carbene adduct of Sc_2C_{82} reveal a new carbide cluster metallofullerene with the unexpected $C_{2v}(5)$-C_{80} cage, that is, $Sc_2C_2@C_{2v}(5)$-C_{80}. More interestingly, DFT calculations and NMR results disclose that the dynamic motion of the internal Sc_2C_2 cluster depends strongly on temperature. At 293 K, the cluster is fixed inside the cage with two nonequivalent Sc atoms on the mirror plane, thereby leading to C_s symmetry of the whole molecule. However, when the temperature increases to 413 K, the ^{13}C and ^{45}Sc NMR spectra show that the cluster rotates rapidly inside the $C_{2v}(5)$-C_{80} cage, featuring two equivalent Sc atoms and weaker metal−cage interactions.

The interior of fullerenes can host various atoms, molecules and clusters, forming endofullerenes. Among them, endohedral metallofullerenes (EMFs), that is, fullerenes with metallic species inside, have attracted broad attention because of their unique structures, novel properties, and many potential applications in such fields as materials science, catalysis, photovoltaics, and biomedicines.[1]

In EMFs, charge transfer from the internal metallic species to the fullerene cage takes place. It is an interesting question whether the metals are firmly bonded to the specific cage carbons. In many cases, the metal atoms or the metallic cluster move rapidly inside the fullerene cage.[2] Accordingly, it has been a long-time dream that the free rotation of the 'untouchable' metallic clusters can be controlled using some methods.[1e] Recent results showed that exohedral functionalization of EMFs can, to a certain degree, fulfill this goal. For example, the three-dimensional rotation of the two La atoms in $La_2@I_h$-C_{80} is reduced to a two-dimensional motion when the EMF is disilylated, and the motion is halted completely in the open-cage derivative $La_2@I_h$-C_{80}Ad.[3] However, as the chemical modification alters the electronic and geometrical structures of pristine EMFs, other techniques become desirable. Herein, we report our recent findings achieved during the structural characterization of a Sc_2C_{82} isomer[4] that (i) Sc_2C_{82} is actually a carbide EMF; (ii) formation of the unexpected $C_{2v}(5)$-C_{80} cage is selectively templated by the internal Sc_2C_2 cluster; (iii) the dynamic motion of the Sc_2C_2 cluster inside the cage is temperature sensitive, thus providing a new method for controlling the motions of the internal metallic species in EMFs in addition to chemical functionalization.

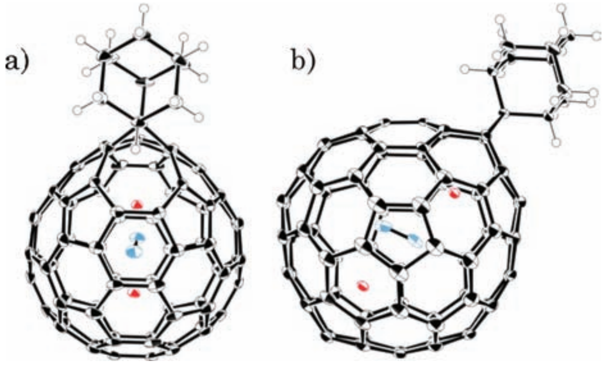

Figure 1. ORTEP drawing of $Sc_2C_2@C_{2v}(5)$-C_{80}Ad with thermal ellipsoids shown at the 50% probability level; (a) front view, (b) side view.

The Sc-containing EMFs are attractive not only because of the high production yield of some species but also because of the diversity of the metallic species that can be encapsulated.[5] To date, one or two Sc atoms, scandium carbide (Sc_2C_2/Sc_3C_2/Sc_4C_2), scandium nitride (Sc_3N), scandium oxide (Sc_2O/Sc_3O_2/ Sc_4O_3), scandium cyanide (Sc_3CN), and even scandium sulfide (Sc_2S) are all found for Sc-EMFs.[5] However, structures of many isomers of Sc-EMFs remain undetermined. Because two carbon atoms, instead of constructing the fullerene cage, can be encapsulated with metals forming carbide clusters, structural identification of Sc-EMFs is fairly important and sometimes troublesome.

Single crystallography is certainly the most reliable method for structural determination. However, the spherical shapes of fullerenes and EMFs have hindered direct X-ray diffraction (XRD) characterization because the molecules rotate rapidly in the crystal lattice. To solve this problem, Sc_2C_{82} was first functionalized with adamantylidene carbene (Ad) to obtain the cycloadducts. Then, single crystals of a monoadduct isomer suitable for X-ray measurement were obtained by a diffusion method; its structure is firmly established, as shown in Figure 1. Two C atoms

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and two Sc atoms are encaged inside the cage originating from $C_{2v}(5)$-C_{80}. The Ad group adds to a [6,6]-junction close to one Sc atom, resulting in an open-cage structure.

Among the seven isomers of C_{80} satisfying the isolated pentagon rule (IPR), the $C_{2v}(5)$-C_{80} cage has never been expected to encapsulate a metal, or any kinds of metallic species known for EMFs to date.[6] Actually, the $C_{2v}(5)$-C_{80} was only obtained recently for the trifluoromethyl derivatives of C_{80}.[7] Experimentally, the $D_{5h}(6)$ and $I_h(7)$ isomers are always found for cluster C_{80}-EMFs, such as $Sc_3N@C_{80}$,[5c] $Sc_3C_2@C_{80}$,[5b] and even $Sc_4O_3@C_{80}$,[5d] while $C_{2v}(3)$-C_{80} is suitable for encapsulating a single metal such as La[8a] or Yb.[8b]

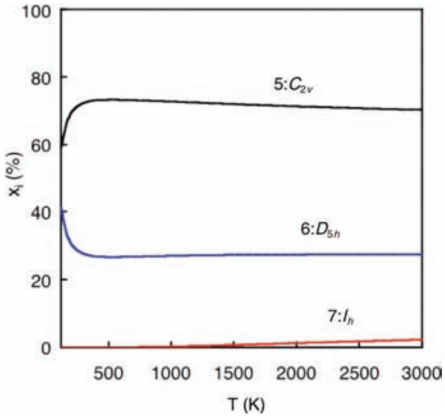

Figure 2. Temperature dependence of the relative populations (molar fractions) for $Sc_2C_2@C_{2v}(5)$-C_{80}, $Sc_2C_2@D_{5h}(6)$-C_{80} and Sc_2C_2-$@I_h(7)$-C_{80} isomers.

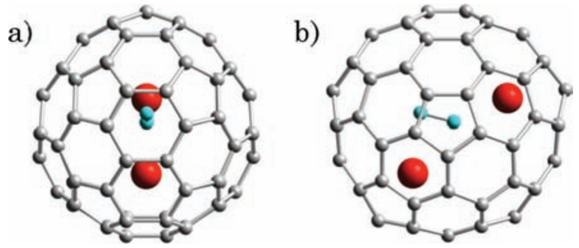

Figure 3. Optimized structure of $Sc_2C_2@C_{2v}(5)$-C_{80} with a fixed Sc_2C_2 cluster; (a) front view, (b) side view. This conformation is lowest in energy and generates the ^{13}C NMR pattern shown in Figure 4a.

To seek explanation for the X-ray structure of $Sc_2C_2@C_{2v}(5)$-C_{80}, we performed density functional theory calculations[13] on the relative stabilities of the three above-mentioned C_{80}-isomers [$C_{2v}(5)$, $D_{5h}(6)$, and $I_h(7)$] encapsulating a Sc_2C_2 cluster. The optimized structure of $Sc_2C_2@C_{2v}(5)$-C_{80} is consistent with the X-ray one. When the Sc_2C_2 cluster is encapsulated, $C_{2v}(5)$ becomes 0.27 and 7.58 kcal/mol more stable than the $D_{5h}(6)$ and $I_h(7)$ isomers, respectively. Because EMFs are formed at extremely high temperatures, the entropical influence on the Gibbs energy cannot be ignored in stability evaluations.[10,11] Thus, in order to consider the thermal/entropic contributions to the relative isomeric concentrations,[12] the Gibbs energy terms were evaluated using the rigid rotor and harmonic oscillator (RRHO) partition functions combined with the fluctuating encapsulate model (FEM) approach.[13] As Figure. 2 shows, $Sc_2C_2@C_{2v}(5)$-C_{80} always prevail among the three isomers at any relevant temperature.

It is interesting to find that the most stable structure of $Sc_2C_2@C_{80}$ involves the encapsulated Sc_2C_2 moiety being fixed, forming a bent structure with two nonequivalent Sc atoms on the mirror plane (Figure 3). Other structures with different Sc_2C_2 conformations are higher in energy, even by 23.3 kcal/mol. Considering the above discussions, it is reasonable to speculate that the $C_{2v}(5)$-C_{80} is selectively templated by the Sc_2C_2 cluster. On the basis of our theoretical calculation, the formal charge density of the compound of current study $Sc_2C_2@C_{2v}(5)$-C_{80} can be described as $(Sc_2C_2)^{4+}C_{80}{}^{4-}$, while in $Sc_3N@C_{80}$ and $La_2@C_{80}$ are $(Sc_3N)^{6-}C_{80}{}^{6+}$ and $(La_2)^{6+}C_{80}{}^{6-}$, respectively. This would be the main reason for the selective formation of the C_{2v}-C_{80} cage.

Variable-temperature nuclear magnetic resonance (NMR) spectrometry provides more interesting results: motional behavior of the Sc_2C_2 cluster is temperature-dependent. A ^{13}C-enriched sample of $Sc_2C_2@C_{2v}(5)$-C_{80} was used to enable the detection of all possible ^{13}C NMR signals, including that from the internal C_2 unit. As Figure 4a shows, the ^{13}C NMR spectrum measured at 298 K displays 39 full-intensity lines and 2 half-intensity lines in the aromatic region, which can be ascribed to the sp^2-hybridized cage carbons. This pattern conflicts with that of an idealized $C_{2v}(5)$-C_{80} which displays a [18 × 2C; 4 × 1C] pattern.[6] Nevertheless, the observed spectrum is consistent with the structure depicted in Figure 3 showing that the Sc_2C_2 cluster is fixed with the two Sc atoms on the mirror plane. The Sc atoms interact strongly with the cage carbons and influence their

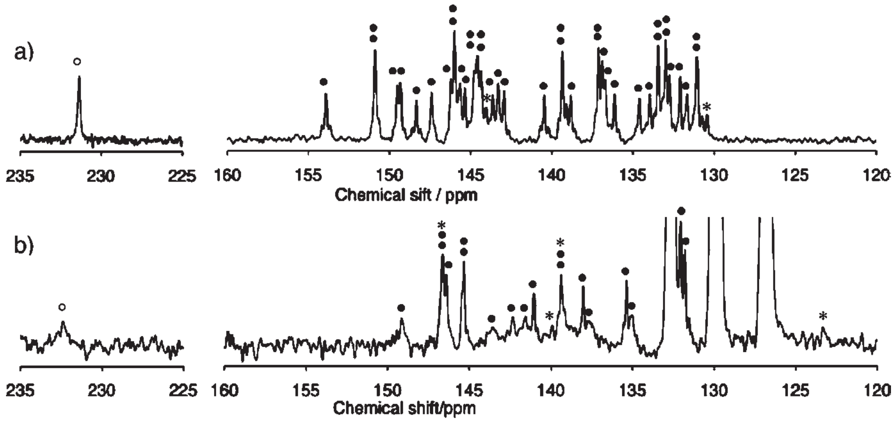

Figure 4. ^{13}C NMR spectra of $Sc_2C_2@C_{2v}(5)$-C_{80} measured (a) in CS_2 at 298 K [39 × 2C; 2 × 1C] and (b) in 1,2-dichlorobenzene at 413 K [18 × 2C; 4 × 1C]. The signal from the C_2 moiety of Sc_2C_2 is marked with an open circle; * indicates half intensity.

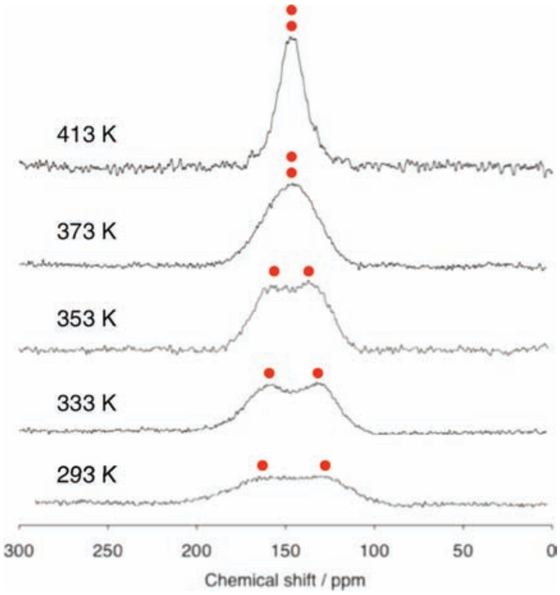

Figure 5. VT ^{45}Sc NMR spectra of $Sc_2C_2@C_{2v}(5)$-C_{80}.

chemical shifts. The signal ascribed to the encapsulated C_2 unit is observed at 231.5 ppm, which is similar to those of $Sc_2C_2@C_{84}$ (249.2 ppm) and $Sc_2C_2@C_{82}$ (253.2 ppm) previously reported.[14] The single peak indicates two equivalent internal carbon atoms, also consistent with the most stable structure shown in Figure 3.

Interestingly, we found that the fixed carbide cluster is rotatable upon heating. When the temperature increases to 413 K, the ^{13}C NMR spectrum changes from the [39 × 2C; 2 × 1C] pattern to a [18 × 2C; 4 × 1C] pattern (Figure 4b), which unambiguously originates from the $C_{2v}(5)$-C_{80} cage,[6] requesting the Sc_2C_2 cluster move rapidly inside the cage.

Variable-temperature (VT) NMR results of the ^{45}Sc nuclei provide additional information about the dynamic motions of the internal cluster. Figure 5 portrays the spectra. Two distinct signals of equal intensity are observed at 293 K, indicating the presence of two different scandium atoms, which agrees perfectly with the ^{13}C NMR results and the calculations. The peak separation is 30 ppm, showing that the magnetic environments of the two Sc nuclei are very different. Separation of two peaks is observable continuously when the temperature is lower than 353 K, but they coalesce into one at higher temperatures, implying that the two scandium atoms became equivalent. These clearly elucidate the temperature-dependent character of the motions of the Sc_2C_2 cluster. The energy of the inversion barrier is estimated to be $\Delta G^* = 15.1$ kcal/mol ($T_c = 373$ K, $\delta\nu = 5100$ Hz), using the equation: $\Delta G^* = RT_c[22.96 + \ln(T_c/\delta\nu)]$ (cal/mol), where T_c = coalescence temperature in K and $\delta\nu$ = chemical shift difference in Hz.

In conclusion, the structure of a Sc_2C_{82} isomer was determined unambiguously to be a carbide cluster metallofullerene $Sc_2C_2@C_{2v}(5)$-C_{80} instead of $Sc_2@C_{82}$. It is reported herein for the first time that the motions of the internal Sc_2C_2 cluster are highly temperature-dependent. At 335 K or lower, the cluster is fixed in the cage. The metals interact strongly with the specific cage carbons, engendering C_s symmetry for the whole molecule. Above this temperature, however, the cluster goes over a rotation barrier and then rotates rapidly inside the cage developing a C_{2v} symmetry of the molecule. In view of this characteristic, $Sc_2C_2@C_{2v}(5)$-C_{80} is useful as a molecular thermo-indicator in nanoscience. This is the first reported observation showing that the symmetry of the whole molecule of an EMF is affected by internal metallic species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. HPLC profiles, mass spectrum, UV−vis−NIR spectrum, NMR spectra, summary of ^{13}C NMR chemical shifts, calculated results of $Sc_2C_2@C_{2v}(5)$-C_{80}, and X-ray data of $Sc_2C_2@C_{2v}(5)$-C_{80}Ad, and complete ref 9a. This material is available free of charge via the Internet at http://pubs.acs.org.

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