Communication

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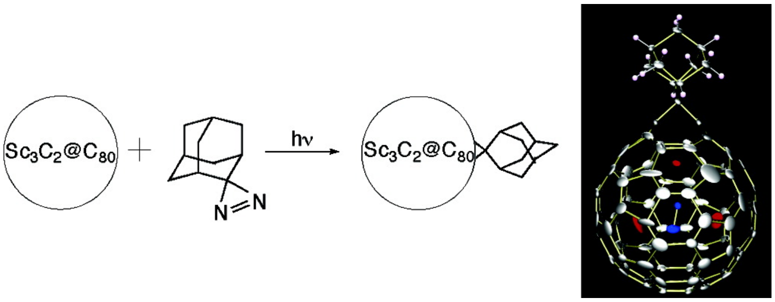

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Structural Determination of Metallofullerene Sc_3C_{82} Revisited: A Surprising Finding

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Endohedral metallofullerenes have attracted wide interest in recent years because of the promising material, catalytic, and biomedical applications.[1−3] The structures and electronic properties of endohedral metallofullerenes have been extensively investigated both experimentally and theoretically.[3] It is widely accepted that the maximum entropy method (MEM)/Rietveld analysis of synchrotron X-ray powder diffraction data is powerful for structural determination of endohedral metallofullerenes.[4,5] Since the first application to $Y@C_{82}$ in 1995,[6] the endohedral structures of representative metallofullerenes, such as $Sc@C_{82}$,[7] $La@C_{82}$,[8] $Eu@C_{82}$,[9] $Gd@C_{82}$,[10] $Sc_2@C_{66}$,[11] $Sc_2@C_{84}$,[12] $La_2@C_{80}$,[13] $Sc_2C_2@C_{84}$,[14] and $Sc_3@C_{82}$,[15] have been determined by the MEM/Rietveld method.[4,5] However, these structures do not always correspond to energy minima or most stable structures.[16−18] For example, the MEM/Rietveld analysis of $Sc_3@C_{82}$ has shown three Sc atoms encapsulated inside a C_{3v} isomer of C_{82} as a trimer with extremely short Sc−Sc distances of 2.33 Å.[15] On the other hand, Kobayashi and Nagase calculated that the endohedral structure is not an energy minimum; it is energetically much more favorable that three Sc atoms are encaged inside another C_{3v} isomer of C_{82} with much longer Sc−Sc distances of 3.6−4.0 Å.[17]

To address the reliability of the widely used MEM/Rietveld method, we report here structural determination of the Sc_3C_{82} molecule by ^{13}C NMR spectroscopy and X-ray single-crystal structure analysis.

As demonstrated for metallofullerenes, such as $La@C_{82}$,[19,20] $Ce@C_{82}$,[21] and $Pr@C_{82}$,[22] ^{13}C NMR spectroscopy is a useful tool for elucidating the endohedral structures. Since Sc_3C_{82} is paramagnetic, we measured the ^{13}C NMR spectrum of its diamagnetic anion in acetone-d_6/CS_2. A total of 16 ^{13}C NMR lines[23] should be observed for the C_{3v} endohedral structure determined by the MEM/Rietveld method. As Figure 1 shows, however, only two lines were observed in the ^{13}C NMR spectrum of the Sc_3C_{82} anion. Apparently, neither C_{3v} nor any other C_{82} isomers satisfy the ^{13}C NMR pattern. Interestingly, the ^{13}C NMR spectrum is very similar to that observed for $Sc_3N@C_{80}$.[24] This suggests that the cage structure of Sc_3C_{82} originates from the I_h isomer of C_{80}, and two C atoms as well as three Sc atoms are encaged inside the C_{80} fullerene. The $Sc_3C_2@C_{80}$ structures found by density functional calculations are shown in panels a and b of Figure 2.[25,26] These structures are 30.2 and 31.9 kcal/mol more stable than the lowest energy $Sc_3@C_{82}$ structure[17] and are 82.6 and 84.3 kcal/mol more stable than the structure optimized by encaging three Sc atoms inside the C_{82} isomer determined by the MEM/Rietveld method, respectively. For $Sc_3C_2@C_{80}$, it was calculated that almost six electrons are transferred from the endohedral Sc_3C_2 part to C_{80} to form a stable closed-shell electronic structure on C_{80}.

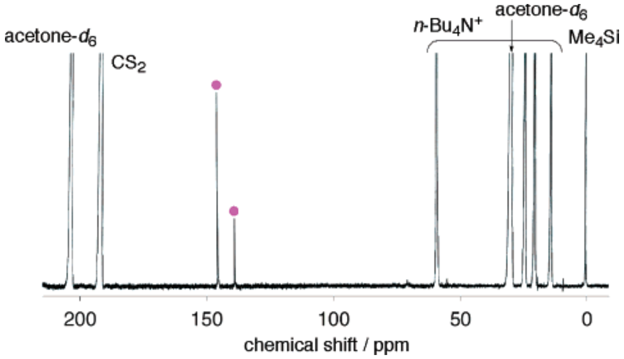

Figure 1. The ^{13}C NMR spectrum of n-$Bu_4N^+[Sc_3C_2@C_{80}]^-$ in acetone-d_6/CS_2 at 298 K.

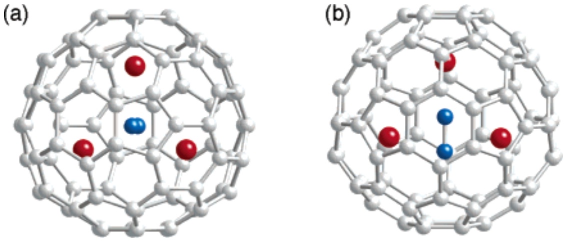

Figure 2. Structures calculated for $Sc_3C_2@C_{80}$.

The analysis of single-crystal X-ray diffraction data of $Sc_3C_2@C_{80}$ was made very difficult by the nearly free rotation of the round $Sc_3C_2@C_{80}$ units in the lattice. Therefore, we have carried out chemical functionalization of the $Sc_3C_2@C_{80}$ molecule by adamantylidene carbene (Ad) to obtain the cycloadduct, $Sc_3C_2@C_{80}$(Ad) (**1**). Irradiation of a 1,2,4-trichlorobenzene/toluene solution of $Sc_3C_2@C_{80}$ and an excess molar amount of 2-adamantane-2,3-[3*H*]-diazirine in a degassed sealed tube at room temperature using a high-pressure mercury arc lamp (cutoff < 350 nm) resulted in the

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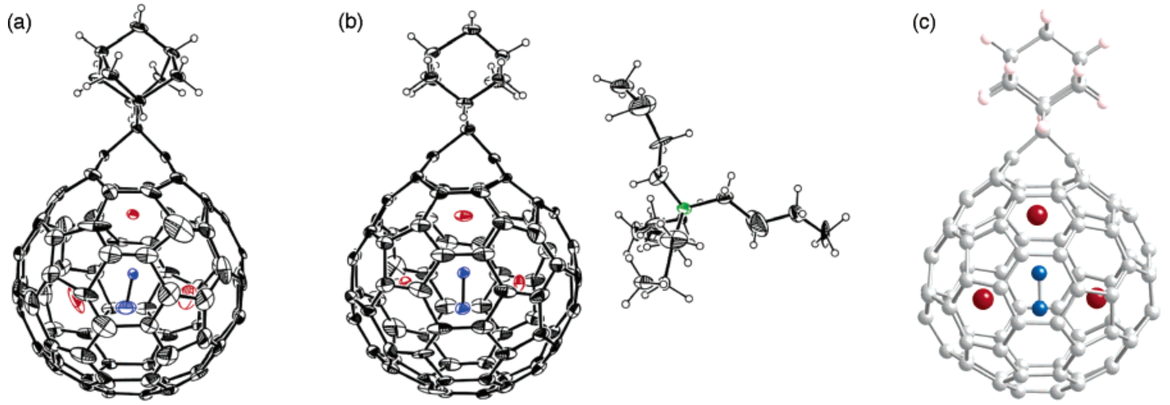

Figure 3. ORTEP drawings of the X-ray single-crystal structures of (a) $Sc_3C_2@C_{80}$(Ad) and (b) n-$Bu_4N^+[Sc_3C_2@C_{80}(Ad)]^-$ with thermal ellipsoids at the 30% probability level, in which one orientation is shown and CS_2 is omitted for clarity. (c) The C_s structure optimized for $Sc_3C_2@C_{80}$(Ad).

formation of **1**, which was purified by preparative HPLC. MALDI-TOF mass analysis of the isolated **1** exhibits a single molecular ion peak. As shown clearly in the X-ray single-crystal structure (Figure 3a), the cycloadduct **1** results from the addition of Ad onto $Sc_3C_2@C_{80}$ (not $Sc_3@C_{82}$). This is also confirmed by the X-ray single-crystal structure analysis of n-$Bu_4N^+[Sc_3C_2@C_{80}(Ad)]^-$, as shown in Figure 3b. As these single-crystal structures show, **1** is formed from the 6,6-addition of Ad. The ^{13}C NMR spectrum of its anion in pyridine-d_5/CS_2 shows that **1** has C_s symmetry (see Supporting Information). These results agree well with the calculated structure shown in Figure 3c.[25]

From the present study, it is obvious that the structure of Sc_3C_{82} is not $Sc_3@C_{82}$ but $Sc_3C_2@C_{80}$. This suggests that the widely used MEM/Rietveld analysis is not reliable enough to determine the structures of metallofullerenes. It may be desirable to re-examine the structures of metallofullerenes determined by the MEM/Rietveld method.

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Supporting Information Available: Experimental details and spectroscopic data for $Sc_3C_2@C_{80}$(Ad). X-ray crystallographic details, including CIF files. The complete lists of authors for refs 19−22 and 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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