Planar Quinary Cluster inside a Fullerene Cage: Synthesis and Structural Characterizations of Sc$_3$NC@C$_{80}$-I$_n$

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Abstract: The endohedral fullerene Sc$_3$NC@C$_{80}$-I$_n$ has been synthesized and characterized; it has an unprecedented planar quinary cluster in a fullerene cage. It is also the first chemical compound in which the presence of an unprecedented (NC)$_3$ trianion has been disclosed. The fascinating intramolecular dynamics in Sc$_3$NC@C$_{80}$-I$_n$ ENABLES the whole molecule to display high polarity and promising ferroelectricity. This finding inspires the possibility that such a planar quinary cluster may be useful in constructing many other endohedral fullerenes.

As the properties of endohedral fullerenes are generally determined by both the encaged species and the parent fullerene cage, it is a challenge for scientists to synthesize different cluster (or molecule) endohedral fullerenes in pursuit of novel electronic and magnetic properties. To date, several types of metal-containing molecules (endohedral fullerenes) have been encaged by both the encaged species and the parent fullerene cage, mined by both the encaged species and the parent fullerene cage, respectively. Furthermore, the nature of the encapsulated species has an influence on the metallic properties of fullerene cages. On the other hand, fullerene cages can be considered templates for the synthesis of more and more endohedral fullerene clusters. Thus, the design and discovery of other inner templates are crucial for the synthesis of more and more endohedral fullerenes.

In 2005, an ideal capsule for accommodating some scarce and unstable species was predicted by density functional theory (DFT) calculations to be obtained by fullerene encapsulation. Recently, Dorn et al. detected a Sc$_3$NC$_4$ compound with a mass-to-charge ratio of 1121 from the solvate molecules of benzene have been omitted. Bond distances (Å) in the Sc$_3$NC moiety: N−C$_1$: 1.193(11); N−Sc$_1$: 2.072(8); N−Sc$_2$: 2.138(5); N−Sc$_3$: 2.182(6); C−Sc$_1$: 2.252(12); C−Sc$_2$: 2.048(11). Angles (deg) in the Sc$_3$NC moiety: Sc$_1$−N−Sc$_2$: 102.3(3); Sc$_1$−N−Sc$_3$: 110.8(3); C$_1$−N−Sc$_2$: 79.5(6); C$_1$−N−Sc$_3$: 67.5(6).

Figure 1. View of the structure of Sc$_3$NC@C$_{80}$-I$_n$·Ni$_{10}$(OEP). For clarity, the solvate molecules of benzene have been omitted. Bond distances (Å) in the Sc$_3$NC moiety: N−C$_1$: 1.193(11); N−Sc$_1$: 2.072(8); N−Sc$_2$: 2.138(5); N−Sc$_3$: 2.182(6); C−Sc$_1$: 2.252(12); C−Sc$_2$: 2.048(11). Angles (deg) in the Sc$_3$NC moiety: Sc$_1$−N−Sc$_2$: 102.3(3); Sc$_1$−N−Sc$_3$: 110.8(3); C$_1$−N−Sc$_2$: 79.5(6); C$_1$−N−Sc$_3$: 67.5(6).

was isolated by multistage high-performance liquid chromatography (HPLC). The purified sample exhibited a strong molecular ion peak at m/z 1121 in the mass spectrum, accounting for a chemical composition of Sc$_3$NC$_4$ [see the Supporting Information (SI)].

Sc$_3$NC$_4$ was definitely confirmed as the endohedral fullerene Sc$_3$NC@C$_{80}$-I$_n$ by single-crystal X-ray diffraction. A black crystal of Sc$_3$NC@C$_{80}$-I$_n$·Ni$_{10}$(OEP)·1.5C$_6$H$_6$ was obtained by diffusing a benzene solution of Sc$_3$NC$_4$ into a benzene solution of Ni$_{10}$(OEP). Figure 1 shows a drawing of Sc$_3$NC@C$_{80}$-I$_n$ with the adjacent Ni$_{10}$(OEP) molecule. The crystallographically determined structure unambiguously reveals the presence of the C$_{80}$-I$_n$ cage, which has been observed for many C$_{80}$-based endohedral fullerenes. In the endohedral Sc$_3$NC moiety, the N atom is located in the center of the cluster, and the C atom resides on one side of the triangle formed by the scandium atoms. The N−C bond length is 1.193(11) Å, and the N−Sc$_1$, N−Sc$_2$, and N−Sc$_3$ bond distances are 2.072(8), 2.138(5), and 2.182(6) Å, respectively. Since the sum of the four angles around the central nitrogen is 360.1° (102.3 + 110.8 + 79.5 + 67.5), these five atoms are organized in a plane with approximate C$_2$ symmetry. Previous studies have revealed several planar endohedral clusters, which exist in the trimetallic nitride form in the cases of Sc$_3$N@C$_{80}$, Sc$_3$N@C$_{78}$, Sc$_3$N@C$_{68}$, and Lu$_3$N@C$_{80}$. The Sc$_3$NC moiety is the first planar quinary cluster inside a fullerene cage, suggesting that such a planar cluster might be another important template in the construction of endohedral fullerenes. By the way, the Sc$_3$C$_2$@C$_{80}$ cage also has a quinary Sc$_3$C$_2$ endocluster that preferably adopts trigonal bipyramidal structure, as disclosed by X-ray diffraction and $^{13}$C NMR and ESR spectroscopy experiments.
The Sc$_3$NC@C$_{80}$ molecule was then characterized by $^{13}$C NMR spectroscopy. Two signals at 137.7 ppm and 144.9 ppm in a 1:3 intensity ratio were observed (Figure 2a). This is the unique $^{13}$C NMR pattern of the C$_{80}$ cage (20 triphenylenic sites and 60 corannulenic sites). Fasically, such a $^{13}$C NMR pattern is similar to that of Sc$_3$N@C$_{80}$, suggesting that the Sc$_3$NC and Sc$_3$N endocusters have similar intramolecular dynamics, i.e., the Sc$_3$NC or Sc$_3$N endocluster undergoes constant rotation within the C$_{80}$ cage at room temperature. According to this result, the $^{45}$Sc NMR spectra of Sc$_3$N@C$_{80}$, Sc$_3$NC@C$_{80}$, and CeSc$_2$N@C$_{80}$, which exhibit a single $^{45}$Sc signal arising from equivalent Sc nuclei, suggest that the $^{45}$Sc NMR spectrum for Sc$_3$NC@C$_{80}$ suggests the inhomogeneous electronic environment for the three Sc atoms in the Sc$_3$NC cluster. In view of the near 1:3 rotation of the Sc$_3$NC cluster revealed by the $^{13}$C NMR spectrum, the unique $^{45}$Sc NMR result should be explained by the compact Sc$_3$NC moiety and confined rotation of the NC unit, which rotates simultaneously with the Sc nuclei, maintaining the near C$_{2v}$ symmetry as illustrated in Figure 1. Such peculiar dynamics of the endohedral Sc$_3$NC cluster enable the whole molecule to display unusually high polarity induced by the C$_{2v}$-symmetric [Sc$_3$NC]$^{6-}$ moiety. Consequently, it is reasonable to envision that solids of this novel endofullerene would display ferroelectricity.

We then performed DFT calculations to further describe the structure and electronic properties of Sc$_3$NC@C$_{80}$. Figure 2c shows the BLYP/DNP-optimized structure of Sc$_3$NC@C$_{80}$, whose encaged Sc$_3$NC moiety has a planar C$_{2v}$-symmetric structure with the NC unit surrounded by three Sc atoms. The ground state of Sc$_3$NC@C$_{80}$ adopts a closed-shell electronic configuration. Analyses of the Kohn–Sham wave functions of Sc$_3$NC@C$_{80}$ revealed its valence state of [Sc$_3$NC]$.^{6-}$ This is the first report of this unprecedented NC trianion, which is stabilized by forming a Sc$_3$NC cluster that is then encapsulated into a C$_{80}$ cage. FTIR spectra of Sc$_3$NC@C$_{80}$, Sc$_3$N@C$_{80}$, and Sc$_3$C$_2$@C$_{80}$-I$_h$ are shown in Figure 3 for comparison. The tangential cage modes of Sc$_3$NC@C$_{80}$, ranging from 1200 to 1600 cm$^{-1}$ and the radial cage modes at $\sim$500 cm$^{-1}$ exhibit a high resemblance to those of metallofullerenes with C$_{2v}$-I$_h$. The signals at 660 and 672 cm$^{-1}$ are ascribed to asymmetric C$_{80}$-dominated v$_{as}$(Sc–NC) modes. The N-dominated v$_{as}$(Sc–NC) modes at $\sim$574 cm$^{-1}$ are too weak to be discernible in the experimental spectrum. For Raman spectra, their C$_{2v}$-I$_h$ cage modes between 1200 and 1600 cm$^{-1}$ are very similar. However, in the low-wavenumber range, a group of lines appears at $\sim$468 cm$^{-1}$, accounting for the N-dominated $\delta$(Sc–NC–Sc) bending modes and $\nu$(Sc–NC) stretch modes, which are absent or hardly discernible in Sc$_3$N@C$_{80}$ and Sc$_3$C$_2$@C$_{80}$-I$_h$.

The redox properties of Sc$_3$NC@C$_{80}$ were investigated by cyclic voltammetry (CV). The first oxidation potential $\alpha_{E1}$ was observed at 0.6 V, while two reduction potentials, $\alpha_{E2}$ and $\alpha_{E3}$, appeared at $\sim$1.05 and $\sim$1.68 V, respectively. Both the first reduction and first oxidation steps are reversible. The electrochemical energy gap of Sc$_3$NC@C$_{80}$ is 1.65 V, which is 0.21 V smaller than that of Sc$_3$N@C$_{80}$ ($\alpha_{E1} = 0.62$ V, $\alpha_{E2} = -1.24$ V). While Sc$_3$NC@C$_{80}$ is more electrophilic than Sc$_3$N@C$_{80}$, the two compounds have similar electron-donating abilities.

In conclusion, we have synthesized and characterized an unusual endohedral fullerene, Sc$_3$NC@C$_{80}$, which contains the first reported planar quinary cluster in a fullerene cage. It is also the first chemical compound in which the presence of an unprecedented NC$^-$ trianion has been disclosed. The fascinating intramolecular dynamics in Sc$_3$NC@C$_{80}$ enables the whole molecule to display high polarity and promising ferroelectricity. This finding inspires the possibility that such a planar quinary cluster may serve as a very promising template for the construction of various endohedral fullerenes.

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**Supporting Information Available:** Experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.
having an endohedral C atom in the center of whole molecule was also calculated (see the SI). The results showed that this isomer has a lower energy than the crystallographically determined structure of Sc3NC@C80-Ih. Thus, the Sc3CN@C80-Ih isomer maybe another important endofullerene waiting for experimental proof.