

Planar Quinary Cluster inside a Fullerene Cage: Synthesis and Structural Characterizations of $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$

Tai-Shan Wang,[†] Lai Feng,[†] Jing-Yi Wu,[†] Wei Xu,[†] Jun-Feng Xiang,[†] Kai Tan,[‡] Yi-Han Ma,[†] Jun-Peng Zheng,[†] Li Jiang,[†] Xin Lu,^{*,‡} Chun-Ying Shu,^{*,†} and Chun-Ru Wang^{*,†}

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Beijing 100190, China, and State Key Laboratory of Physical Chemistry of the Solid Surface and Center for Theoretical Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Received August 31, 2010; E-mail: xinlu@xmu.edu.cn; shucy@iccas.ac.cn; crwang@iccas.ac.cn

Abstract: The endohedral fullerene $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$ 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 $(\text{NC})^{3-}$ trianion has been disclosed. The fascinating intramolecular dynamics in $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$ 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.¹ To date, several types of metal-containing clusters, including metal atom(s), metal nitride, metal carbide, metal oxide, metal sulfide, etc., have been found to be encaged in metallofullerenes.^{1,2} The boom of these endofullerenes can be ascribed to the inner-template effect arising from the above endohedral clusters.² Thus, the design and discovery of other inner templates are crucial for the synthesis of more and more endohedral fullerenes. On the other hand, fullerene cages can be considered as ideal capsules to accommodate some scarce and unstable species that are not viable under normal chemical conditions.¹ In 2005, an unusual C_2^{3-} trianion coordinated by three Sc^{3+} cations in the endofullerene $\text{Sc}_3\text{C}_2@C_{80}$ was disclosed.^{3a-c} A recently successful case is the discovery of an unprecedented C_2^{6-} hexaanion entrapped in the endofullerene $\text{Sc}_4\text{C}_2@C_{80}$.^{3d,e} In spite of the harsh synthetic conditions, it is envisioned that additional rare chemical moieties could be obtained by means of fullerene encapsulation. Recently, Dorn et al.^{3f} detected a $\text{Sc}_3\text{NC}_{81}$ compound with a mass-to-charge ratio of 1121 from the soot of an arc discharge, and this species was predicted by density functional theory (DFT) calculations to have the $\text{Sc}_3\text{NC}@C_{80}$ structure.^{3f} Herein, we report the definite experimental studies of this novel endohedral fullerene $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$, which has an unprecedented planar Sc_3NC endohedral cluster containing the $(\text{NC})^{3-}$ trianion. The structure and electronic properties of this novel endohedral fullerene have been well-characterized by X-ray crystallography and various spectroscopic techniques (¹³C NMR, IR, Raman) as well as quantum-chemical calculations.

$\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$ was prepared by the arc-discharge method under a mixed atmosphere of 6 Torr N_2 and 200 Torr He. The sample

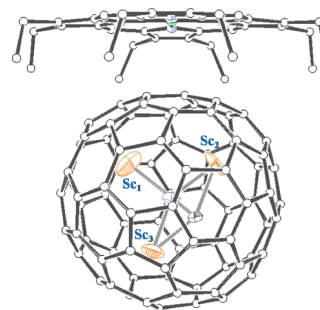


Figure 1. View of the structure of $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h \cdot \text{Ni}^{\text{II}}(\text{OEP}) \cdot 1.5\text{C}_6\text{H}_6$. For clarity, the solvate molecules of benzene have been omitted. Bond distances (Å) in the Sc_3NC moiety: N–C, 1.193(11); N–Sc1, 2.072(8); N–Sc2, 2.138(5); N–Sc3, 2.182(6); C–Sc2, 2.252(12), C–Sc3, 2.048(11). Angles (deg) in the Sc_3NC moiety: Sc1–N–Sc2, 102.3(3); Sc1–N–Sc3, 110.8(3); C–N–Sc2, 79.5(6); C–N–Sc3, 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 $\text{Sc}_3\text{NC}_{81}$ [see the Supporting Information (SI)].

$\text{Sc}_3\text{NC}_{81}$ was definitely confirmed as the endohedral fullerene $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$ by single-crystal X-ray diffraction.⁴ A black crystal of $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h \cdot \text{Ni}^{\text{II}}(\text{OEP}) \cdot 1.5\text{C}_6\text{H}_6$ (OEP = octaethylporphyrin) was obtained by diffusing a benzene solution of $\text{Sc}_3\text{NC}_{81}$ into a benzene solution of $\text{Ni}^{\text{II}}(\text{OEP})$. Figure 1 shows a drawing of $\text{Sc}_3\text{NC}@C_{80}\text{-}I_h$ with the adjacent $\text{Ni}^{\text{II}}(\text{OEP})$ molecule. The crystallographically determined structure unambiguously reveals the presence of the $\text{C}_{80}\text{-}I_h$ cage, which has been observed for many C_{80} -based endohedral fullerenes.^{2a,3a,e,5} In the endohedral Sc_3NC 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–Sc1, N–Sc2, and N–Sc3 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_{2v} symmetry. Previous studies have revealed several planar endohedral clusters, which exist in the trimetallic nitride form in the cases of $\text{Sc}_3\text{N}@C_{80}$, $\text{Sc}_3\text{N}@C_{78}$, $\text{Sc}_3\text{N}@C_{68}$, and $\text{Lu}_3\text{N}@C_{80}$.¹ The Sc_3NC 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 $\text{Sc}_3\text{C}_2@C_{80}\text{-}I_h$ also has a quinary Sc_3C_2 endocluster that preferentially adopts trigonal bipyramidal structure, as disclosed by X-ray diffraction^{3b} and ¹³C NMR and ESR spectroscopy experiments.⁶

[†] Institute of Chemistry.

[‡] Xiamen University.

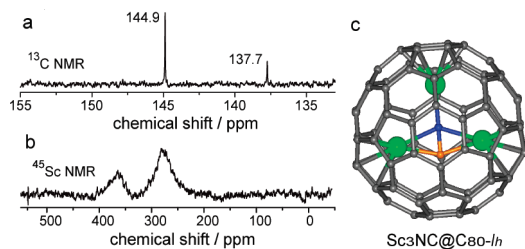


Figure 2. (a) Experimental ^{13}C NMR spectrum (CS_2 , 150 MHz) of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$. (b) Experimental ^{45}Sc NMR spectrum (CS_2 , 145 MHz) of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$. D_2O inside of a capillary was used as an internal lock. (c) Optimized structure of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$. Green balls represent Sc atoms. Blue and orange balls denote N and C atoms of the inner NC unit, respectively.

The $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ 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 in the spectrum were clearly observed (Figure 2a). This is the unique ^{13}C NMR pattern of the $C_{80}\text{-I}_h$ cage (20 triphenylenic sites and 60 corannulenic sites). Fascinatingly, such a ^{13}C NMR pattern is similar to that of $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$,^{2a} suggesting that the Sc_3NC and Sc_3N endoclusters have similar intramolecular dynamics, i.e., the Sc_3NC or Sc_3N endocluster undergoes constant rotation within the $C_{80}\text{-I}_h$ cage at room temperature. In accordance with such intramolecular dynamics, the ^{45}Sc NMR spectrum of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ exhibits two signals in a 1:2 intensity ratio at room temperature; this result is different from the reported ^{45}Sc NMR spectra of $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$ ^{2a} and $\text{CeSc}_2\text{N}@C_{80}\text{-I}_h$,^{5b} which exhibit a single ^{45}Sc signal arising from equivalent Sc nuclei. The ^{45}Sc NMR spectrum for $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ suggests the inhomogeneous electronic environment for the three Sc atoms in the Sc_3NC cluster. In view of the free rotation of the Sc_3NC cluster revealed by the above ^{13}C NMR spectrum, the unique ^{45}Sc NMR result should be explained by the compact Sc_3NC 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_3NC cluster enable the whole molecule to display unusually high polarity induced by the C_{2v} -symmetric $[\text{Sc}_3\text{NC}]^{6+}$ moiety. Consequently, it is reasonable to envision that solids of this novel endofullerene would display ferroelectricity.⁷

We then performed DFT calculations to further describe the structure and electronic properties of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$. Figure 2c shows the BLYP/DNP-optimized structure of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$,⁸ whose encaged Sc_3NC moiety has a planar C_{2v} -symmetric structure with the NC unit surrounded by three Sc atoms. The ground state of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ adopts a closed-shell electronic configuration. Analyses of the Kohn–Sham wave functions of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ revealed its valence state of $[\text{Sc}^{3+}]_3[\text{NC}]^{3-}@[\text{C}_{80}]^{6-}$. This is the first report of this unprecedented NC trianion, which is stabilized by forming a Sc_3NC cluster that is then encapsulated into a C_{80} cage.

FTIR spectra of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$, $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$, and $\text{Sc}_3\text{C}_2@C_{80}\text{-I}_h$ are shown in Figure 3 for comparison. The tangential cage modes of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ ranging from 1200 to 1600 cm^{-1} and the radial cage modes at ~ 500 cm^{-1} exhibit a high resemblance to those of metallofullerenes with $C_{80}\text{-I}_h$.⁹ The signals at 660 and 672 cm^{-1} are ascribed to asymmetric C_{NC} -dominated $\nu_{\text{as}}(\text{Sc}\text{--}\text{NC})$ modes. The N-dominated $\nu_{\text{as}}(\text{Sc}\text{--}\text{NC})$ modes at ~ 574 cm^{-1} are too weak to be discernible in the experimental spectrum. For Raman spectra, their $C_{80}\text{-I}_h$ cage modes between 1200 and 1600 cm^{-1} are very similar.⁹ However, in the low-wavenumber range, a group of lines appears at ~ 468 cm^{-1} , accounting for the N-dominated $\delta(\text{Sc}\text{--}\text{NC}\text{--}\text{Sc})$

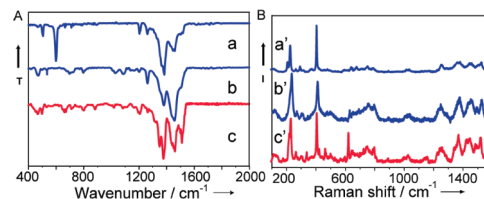


Figure 3. FTIR and Raman spectra of (a, a') $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$, (b, b') $\text{Sc}_3\text{C}_2@C_{80}\text{-I}_h$, and (c, c') $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$. Laser wavelength: 633 nm.

bending modes and $\nu_{\text{s}}(\text{Sc}\text{--}\text{NC})$ stretch modes, which are absent or hardly discernible in $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$ and $\text{Sc}_3\text{C}_2@C_{80}\text{-I}_h$.

The redox properties of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ were investigated by cyclic voltammetry (CV). The first oxidation potential ${}_{\text{ox}}E_1$ was observed at 0.6 V, while two reduction potentials, ${}_{\text{red}}E_1$ and ${}_{\text{red}}E_2$, appeared at -1.05 and -1.68 V, respectively. Both the first reduction and first oxidation steps are reversible. The electrochemical energy gap of $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ is 1.65 V, which is 0.21 V smaller than that of $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$ (${}_{\text{red}}E_1 = 0.62$ V, ${}_{\text{ox}}E_1 = -1.24$ V).^{9a} While $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ is more electrophilic than $\text{Sc}_3\text{N}@C_{80}\text{-I}_h$, the two compounds have similar electron-donating abilities.

In conclusion, we have synthesized and characterized an unusual endohedral fullerene, $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$, 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 $(\text{NC})^{3-}$ trianion has been disclosed. The fascinating intramolecular dynamics in $\text{Sc}_3\text{NC}@C_{80}\text{-I}_h$ 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>.

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