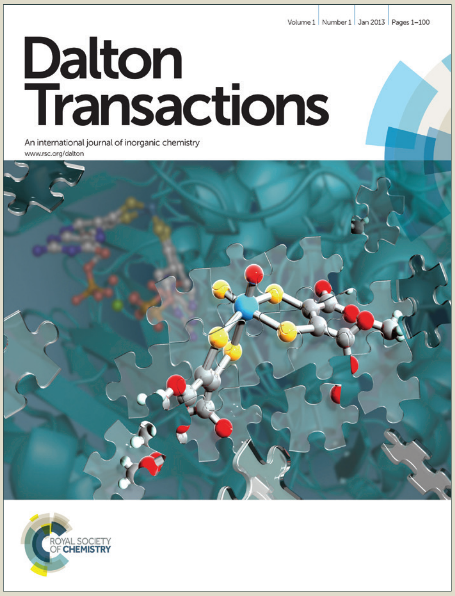
Dalton Transactions

Accepted Manuscript



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Scandium carbide/cyanide alloyed cluster inside fullerene cage: synthesis and structural studies of $Sc_3(\mu_3\text{-}C_2)(\mu_3\text{-}CN)@I_h\text{–}C_{80}$

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A new $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ metallofullerene encaging a scandium carbide/cyanide alloyed cluster was prepared and investigated. $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ was synthesized by arc-discharging method and isolated by HPLC. Its experimental ^{13}C NMR spectrum with two signals clearly confirms an icosahedral C_{80} cage, and theoretically calculated ^{13}C NMR peaks agree well with experimental results. Further theoretical calculations disclosed that the endohedral $\mu_3\text{-}C_2$ and $\mu_3\text{-}CN$ moieties are respectively situated on each side of triangular shape of Sc_3 unit to form a scandium carbide/cyanide alloyed cluster. Kohn-Sham molecular orbtials reveals its electronic structure of $(Sc^{3+})_3(C_2)^{2-}(CN)^{-}@C_{80}{}^{6-}$, in which two anions, $\mu_3\text{-}C_2{}^{2-}$ and $\mu_3\text{-}(CN)^{-}$, construct and stabilize this special molecule together. The FTIR and Raman spectra of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ were analyzed by comparison of experimental and calculated results to further confirm its structure and to uncover cluster-based vibrational modes.

Introduction

Metallofullerenes have attracted broaden interests due to their nesting structures and unique properties.[1-6] The endohedral metal species include Ca, Sc, Ti, Y, La, Gd, Ho, Er, and many other lanthanide elements, which exhibit lots of chemical/physical/biomedical properties, such as paramagnetism, organic semiconductors, cancer drugs, etc.[7-14] In the course of development for metallofullerenes, the introduction of non-metal moieties, i.e., N, C_2, O, S, CN, to endohedral clusters dramatically enhance the yield of metallofullerenes and enormously expand their structures. The extensive endohedrals contain metal nitride (M_3N), metal carbide (M_2C_2, M_3C_2, M_4C_2), metal oxide (M_4O_2, M_4O_3, M_2O), metal sulfide (M_2S), and metal cyanide (M_3CN, MCN).[15-24] Among these endohedral clusters, the non-metal moieties of N, O, S, all have fixed valence states, there are N^{3-}, O^{2-}, and S^{2-}. However, the C_2 and CN moieties both have variable valance. For example, C_2 moiety exhibits divalent $C_2{}^{2-}$ in $Sc_2C_2@C_{84}$, trivalent $C_2{}^{3-}$ in $Sc_3C_2@I_h\text{-}C_{80}$, and even hexavalent $C_2{}^{6-}$ in $Sc_4C_2@I_h\text{-}C_{80}$.[16-18] Whereas the CN moiety are determined to show trivalent $(CN)^{3-}$ in $Sc_3CN@I_h\text{-}C_{80}$, monovalent $(CN)^{-}$ in $YCN@C_{82}$.[23-25] Such varied valence states bring about many novel clusterfullerenes entrapping multi-component, various chemical bonds, and complex structures. Herein, we report the synthesis, isolation, and characterization of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ that has a scandium carbide/cyanide alloyed cluster by means of ^{13}C NMR spectroscopy, DFT calculations, and IR/Raman spectroscopy. Further theoretical analyses disclosed its valence state of $(Sc^{3+})_3(C_2)^{2-}(CN)^{-}@(I_h\text{-}C_{80})^{6-}$, where the carbide moiety $(C_2)^{2-}$ and cyanide moiety $(CN)^{-}$ together construct this unprecedented metallofullerene.

Results and discussion

The target molecule was synthesized by the Krätschmer-Huffman arc-discharging method and isolated by high performance liquid chromatography (HPLC). Briefly, the graphite tubular was first filled with Sc alloy and then evaporated in the arc-discharging generator under the atmosphere of He/N_2. The soot was Soxhlet-extracted with toluene and mixtures of fullerenes and metallofullerenes were collected. Two columns, known as Buckyprep and Buckyprep-M, were employed to isolate and purify the sample (see ESI).

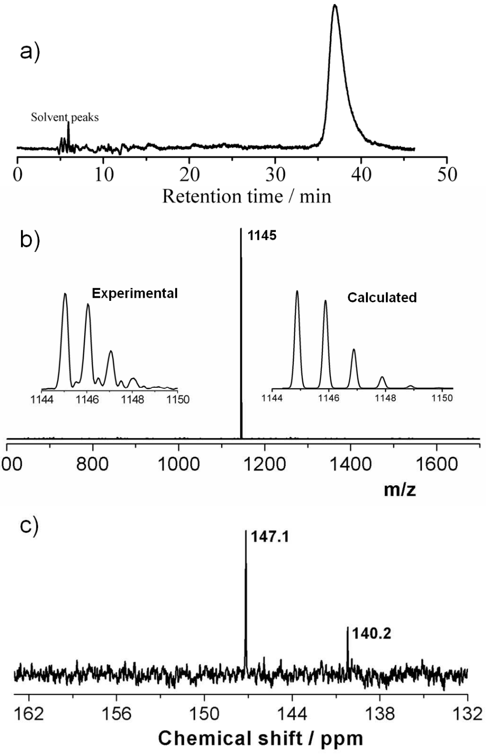

Fig. 1 a) HPLC profile of purified $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ (Φ20×250 mm Buckyprep-M column; flow rate 12 ml/min; toluene as eluent). b) MALDI-TOF mass spectrum of the purified $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$. The insets show the experimental (left) and calculated (right) isotope distributions of $Sc_3C_{83}N$. c) ^{13}C NMR spectrum (CS_2, 150 MHz) of $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$. D_2O inside of a capillary was used as an internal lock.

It should be noted that the retention time of $Sc_3C_{83}N$ is three minutes later that that of reported $Sc_3CN@I_h$-C_{80} in Buckyprep column, see Fig. S3. The purity of the sample was confirmed by both HPLC analysis and the matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrum, see Fig. 1a and 1b. The mass spectrum exhibits a strong molecular ion peak at *m/z* 1145, accounting for the composition of $Sc_3C_{83}N$.

The purified $Sc_3C_{83}N$ was first characterized by ^{13}C NMR spectroscopy. Fig. 1c presents the experimental ^{13}C NMR spectrum of $Sc_3C_{83}N$ in CS_2 at 293 K. Two signals at 140.1 and 147.5 ppm in a 1: 3 intensity ratio can be clearly observed. This ^{13}C NMR spectrum is a characteristic pattern of an I_h-C_{80} cage, which has two types of carbon atoms, i.e., the triphenylenic sites (hexagon-hexagon-hexagon junctions, 20 carbons) and corannulenic sites (hexagon-pentagon-hexagon junctions, 60 carbons).[15,17,18,23] Thus, this molecule can be denoted as $Sc_3C_3N@I_h$-C_{80}, an I_h-C_{80} cage encaging seven-numbered Sc_3C_3N cluster. In addition, this ^{13}C NMR pattern also suggests a constant rotation of endohedral Sc_3C_3N cluster inside fullerene cage at room temperature, which is also found in $Sc_3N@I_h$-C_{80}, $Sc_4O_2@I_h$-C_{80}, $Sc_4C_2@I_h$-C_{80}, $Sc_3CN@I_h$-C_{80}, etc.[14,17,18,23,26] Moreover, the ^{45}Sc NMR spectrum for $Sc_3C_3N@I_h$-C_{80} exhibits only one signal at 195 ppm under room temperature (see ESI). This result not only discloses a constant rotation of inner cluster, but also reveals a high symmetry for Sc_3C_3N cluster that has three equivalent Sc nuclei.

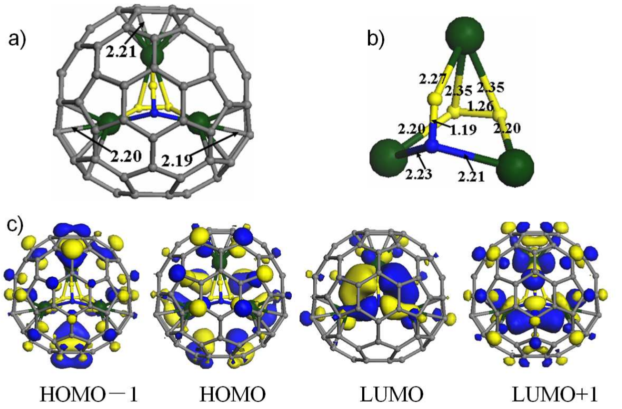

Fig. 2 a) Optimized structure of $Sc_3(C_2)(CN)@I_h$-C_{80}. The shortest distances of Sc-cage are denoted. b) The geometry of $Sc_3(C_2)(CN)$ cluster in $Sc_3(C_2)(CN)@I_h$-C_{80}. The bond lengths of Sc-C and Sc-N are labeled. c) DFT-calculated isodensity surface plots for the HOMO−1, HOMO, LUMO, and LUMO+1 of $Sc_3(C_2)(CN)@I_h$-C_{80}. Green balls represent the Sc atoms, yellow balls the carbon atoms and blue balls the nitride atoms of the inner carbide moiety, the carbon atoms of the I_h-C_{80} cage are represented by gray balls.

The structure of $Sc_3C_3N@I_h$-C_{80} was further investigated by means of density functional theoretical calculations. All of the calculations were performed using the $DMol^3$ code with the generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE).[27-29] Double numerical plus polarization (DNP) basis sets without frozen core were employed for all atoms. Among various possible isomers of $Sc_3C_3N@I_h$-C_{80} we have concerned (see ESI), one isomer with the lowest relative energy and reasonable HOMO-LUMO gap (0.95 eV) has been assigned as the ground-state structure, see Fig. 2a. In optimized structure, the C_2 and CN moieties are respectively located on both sides of Sc_3 triangle and coordinated to three Sc atoms. Therefore, the formula of $Sc_3(\mu_3\text{-}C_2)(\mu_3\text{-}CN)@I_h$-$C_{80}$ can well describe this unique molecule instead. As far as we know, it is the first time to demonstrate a scandium carbide/cyanide alloyed endohedral cluster.

The calculated C−C and C−N bond lengths of endohedral C_2 and CN moieties are 1.26 and 1.19 Å, respectively. The nearest Sc−C_{cage} distances for three Sc are 2.19, 2.20, and 2.21 Å, indicating covalent bonds between Sc and C_{80} cage and their relatively weak interactions. This is the reason for the constant rotation of endohedral Sc_3C_3N cluster inside C_{80} cage to make it homogenous. Moreover, the Sc−$C_{cyanide}$ distance is 2.27 Å, little longer than those of Sc−$N_{cyanide}$ (2.21 and 2.23 Å), as show in Fig. 2b. Interestingly, these bond lengths of Sc−CN are longer than those of $Sc_3CN@I_h$-C_{80}, in which the Sc−$C_{cyanide}$ and Sc−$N_{cyanide}$ distances are 2.08 and 2.10 Å, respectively.[25] In addition, the Sc−$C_{carbide}$ distances are 2.20 and 2.35 Å, which are much longer than Sc−$C_{carbide}$ distances in $Sc_4C_2@I_h$-C_{80} (the nearest Sc−$C_{carbide}$ is 1.96 Å).[26] It can be seen that the bond lengths of Sc-C_2 and Sc-CN are relatively longer and are similar to those of Sc-C_{cage}. These results reveal that, like the flexibility between Sc and C_{80} cage, the Sc atoms and C_2/CN moieties may also have weak interactions.

The electronic structure of $Sc_3(C_2)(CN)@I_h$-C_{80} was also calculated. Detailed analysis of its Kohn-Sham molecular orbtials reveals that it has a valence state of $(Sc^{3+})_3(C_2)^{2-}(CN)^{-}@(C_{80})^{6-}$. The $(C_2)^{2-}$ divalent anion is well known as an important moiety to construct metal carbide clusterfullerenes $M_2C_2@C_{2n}$, such as $Sc_2C_2@C_{84}$, $Sc_2C_2@C_{82}$, $Sc_2C_2@C_{80}$, $Gd_2C_2@C_{92}$, etc.[16,31-33] The $(CN)^{-}$ monoanion is found in metal cyanide clusterfullerene $YCN@C_{82}$.[20] However, in $Sc_3(C_2)(CN)@I_h$-C_{80}, both of the carbide and cyanide units are exiting to build up a complex molecule for the first time. As shown in Fig. 2c, for $Sc_3(C_2)(CN)@I_h$-C_{80}, the two highest occupied molecular orbitals (HOMO and HOMO−1) are mainly localized on the carbon cage. Its HOMO is a hybrid of the 3d orbitals of Sc^{3+} and orbitals of $C_{80}{}^{6-}$ cage, which predicates the existence of the covalent bonds between the Sc^{3+} cations and $C_{80}{}^{6-}$ cage. The lowest unoccupied molecular orbitals (LUMO) are attributed to the covalent dative bondings between the $3d_\pi$ atomic orbitals of Sc^{3+} cations and π^* orbitals of C_2/CN moieties.

The ^{13}C NMR chemical shielding tensors of $Sc_3(C_2)(CN)@I_h$-C_{80} were computed with the hybrid density functional theory at B3LYP level using gauge-independent atomic orbital (GIAO) method.[34-37] Considering the intramolecular dynamics, $Sc_3(C_2)(CN)@I_h$-C_{80} would show two ^{13}C NMR signals arising from I_h-C_{80} cage at room temperature. The calculated NMR peaks locate at 138.7 and 148.5 ppm, which agree well with experimental results, i.e. 140.1 and 147.5 ppm. The ^{13}C NMR chemical shifts of the inner C_2 and CN units were calculated to appear at 223.2 and 174.7 ppm, which were not detected because of the spin-rotation interaction and low signal-to-noise ratio. Table 1 lists the experimental and calculated ^{13}C NMR chemical shifts of several clusterfullerenes with I_h-C_{80} cage. It can be seen that the ^{13}C NMR signals of $Sc_3(C_2)(CN)@I_h$-C_{80} shift to low field compared to those of $Sc_4C_2@I_h$-C_{80} and $Sc_3CN@I_h$-C_{80}.[18,23]

This particularity may be caused by the special $Sc_3(C_2)(CN)$ endohedral cluster.

Table 1. Experimental and calculated ^{13}C NMR chemical shifts of several clusterfullerenes with I_h-C_{80} cage.

clusterfullerene	Experimental (ppm)	Calculated (ppm)
$Sc_3(C_2)(CN)@I_h$-C_{80}	140.1/147.5	138.7/148.5
$Sc_4C_2@I_h$-C_{80}[14]	137.8/144.7	137.7/143.7
$Sc_3CN@I_h$-C_{80}[19]	137.7/144.9	137.3/144.1

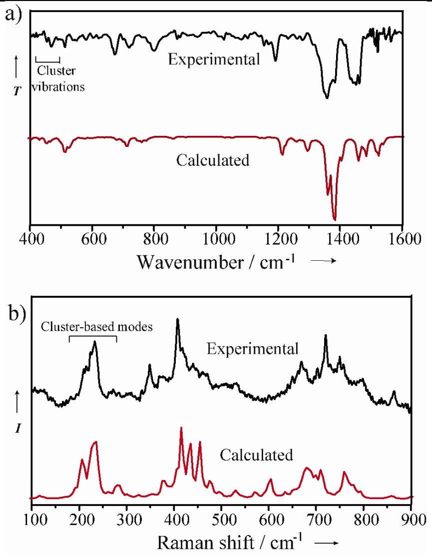

Fig. 3 Experimental and calculated FTIR (a) and Raman (b) spectra of $Sc_3(C_2)(CN)@I_h$-C_{80}. Raman laser wavelength: 633 nm.

Experimental and calculated FTIR spectra of $Sc_3(C_2)(CN)@I_h$-C_{80} are shown in Figure 3a. The tangential cage modes ranging from 1200 cm^{-1} to 1500 cm^{-1} for $Sc_3(C_2)(CN)@I_h$-C_{80} exhibit a high resemblance to those of clusterfullerenes with I_h-C_{80}, such as $Sc_3N@I_h$-C_{80}, $Sc_3C_2@I_h$-C_{80}, $Sc_4C_2@I_h$-C_{80}, and $Sc_3CN@I_h$-C_{80} (see ESI).[18,23,38] However, different from the strong vibrations of asymmetric ν_{as}(Sc−N) modes at 594 cm^{-1} in $Sc_3N@I_h$-C_{80},[38] $Sc_3(C_2)(CN)@I_h$-C_{80} does not present ν_{as}(Sc−N) or ν_{as}(Sc−C) modes due to low symmetry of its complex cluster. Instead of that, a number of vibrations based on $Sc_3(C_2)(CN)$ cluster emerge at ca. 449 and 467 cm^{-1} in experiment. DFT-calculations reveal that these signals ranging from 400 to 500 cm^{-1} can be assigned as C_2 and CN displacements, mostly at 451 and 464 cm^{-1} in theory, see Figure 4a.

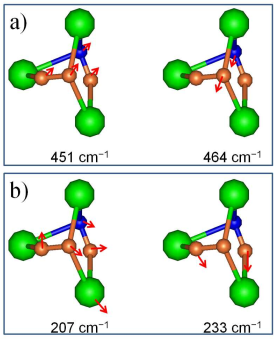

Fig. 4 Selected vibrational modes of calculated FTIR (a) and Raman (b) signals with cluster contribution in $Sc_3(C_2)(CN)@I_h$-C_{80}. The numbers below are computed vibrational frequencies.

The Raman spectrum of $Sc_3(C_2)(CN)@I_h$-C_{80} are shown in Figure 3b. Their C_{80}-I_h cage modes between 1000 cm^{-1} to 1600 cm^{-1} show resemblance with those of $Sc_3N@I_h$-C_{80}, $Sc_3C_2@I_h$-C_{80}, $Sc_4C_2@I_h$-C_{80}, and $Sc_3CN@I_h$-C_{80} (see ESI).[18,23,38] In the low-frequency range (100 to 300 cm^{-1}), the experimental and calculated spectra show high similarity of peaks corresponding to the vibrations form endohedral $Sc_3(C_2)(CN)$ cluster. Theoretical results disclose that these modes are mainly attributed to the frustrated translations of the cluster (calculated at 202, 207, 222 cm^{-1}), and displacements of C_2 and CN moieties (calculated at 228, 233, 237, 277 cm^{-1}), see Figure 4b. The cage breathing modes mixed with cluster vibrations are found ranging from 350 to 500 cm^{-1}.

The redox properties of $Sc_3(C_2)(CN)@I_h$-C_{80} were investigated by cyclic voltammetry (CV) (see SEI). For $Sc_3(C_2)(CN)@I_h$-C_{80}, the first oxidation potential $_{ox}E_1$ was observed at 0.51 V; while two reduction potentials, $_{red}E_1$ and $_{red}E_2$, appear at −0.91 and −1.37 V, respectively. Differently, the $Sc_3NC@I_h$-C_{80} has its $_{ox}E_1$, $_{red}E_1$ and $_{red}E_2$ at 0.6 eV, −1.05 and −1.68 V, respectively.[23]

Conclusions

In summary, a new metallofullerene $Sc_3(C_2)(CN)@I_h$-C_{80} encaging a scandium carbide/cyanide alloyed cluster was synthesized and investigated. The experimental ^{13}C NMR spectrum with two signals clearly confirms its icosahedral C_{80} cage. The calculated NMR peaks agree well with experimental results. Further theoretical calculations disclosed that the μ_3-C_2 and μ_3-CN moieties are respectively situated on both sides of triangular shape of Sc_3 unit to form a scandium carbide/cyanide alloyed endohedral cluster. The electronic structure of $(Sc^{3+})_3(C_2)^{2-}(CN)^{-}@(I_h\text{-}C_{80})^{6-}$ was also concluded, in which two anions of μ_3-$(C_2)^{2-}$ and μ_3-$(CN)^{-}$ play an important role in constructing this special molecule. The FTIR and Raman spectra of $Sc_3(C_2)(CN)@I_h$-C_{80} were also analyzed by comparison of experimental and calculated results to further confirm its structure and also to disclose cluster-based vibrational modes. Due to lack of sample, the attempt to culture its single crystal is not successful. However, these present studies on $Sc_3(C_2)(CN)@I_h$-C_{80} can provide essential inspirations to scientists so as to expand the view of metallofullerene structures and properties.

Acknowledgements

We thank the National Natural Science Foundation (NNSF, 21203205). We also thank Prof. Chunru Wang for his valuable suggestions.

Notes and references

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† Electronic supplementary information (ESI) available: HPLC data, concerned possible isomers of $Sc_3C_3N@I_h$-C_{80}, selected points along the potential energy surface for the rotation of the Sc_3C_3N cluster, cartesian coordinate for ground-state structure of $Sc_3(C_2)(CN)@I_h$-C_{80}. See DOI:10.1039/b000000x/

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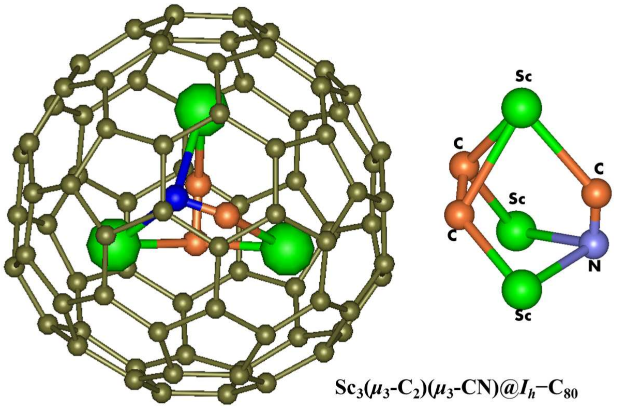

5 A new metallofullerene $Sc_3(C_2)(CN)@I_h\text{-}C_{80}$ encaging a scandium carbide/cyanide alloyed cluster was investigated.