Inorganic Chemistry
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pubs.acs.org/IC

Selective Synthesis, Isolation, and Crystallographic Characterization of LaSc$_2$N@I_h-C$_{80}$

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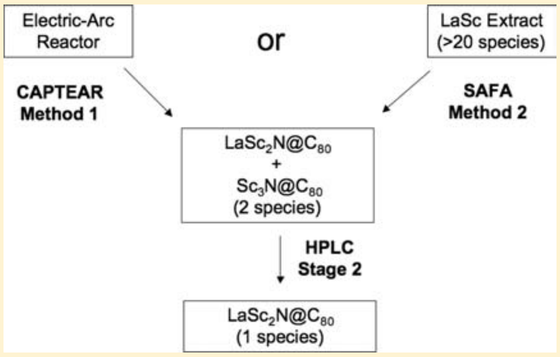
Ⓢ *Supporting Information*

ABSTRACT: The successful preparation and isolation of the mixed-metal endohedral fullerene, LaSc$_2$N@I_h-C$_{80}$, and its structural characterization by single-crystal X-ray diffraction are reported. Results from chemically adjusting plasma temperature, energy, and reactivity (CAPTEAR) experiments indicate that a 10 wt % addition of Cu(NO$_3$)$_2$·2.5H$_2$O to a mixture of La$_2$O$_3$ and Sc$_2$O$_3$ decreases the amount of C$_{60}$ and C$_{70}$ found in soot extracts by an order of magnitude. By combining a stoichiometric 2-fold excess of La to Sc atoms in the plasma reactor, an extract containing a greater abundance of LaSc$_2$N@I_h-C$_{80}$ relative to Sc$_3$N@I_h-C$_{80}$ was obtained. Alternatively, the stir and filter approach (SAFA method) can be used to remove the empty cage fullerenes from a carbon soot sample prepared without using Cu(NO$_3$)$_2$·2.5H$_2$O. LaSc$_2$N@I_h-C$_{80}$ has been characterized by UV/vis absorption spectroscopy and by single-crystal X-ray diffraction. Ordered crystals with nearly identical orientations of the endohedral relative to the porphyrin have been obtained by cocrystallization of LaSc$_2$N@I_h-C$_{80}$ with either Ni^{II}(OEP) or H$_2$(OEP). The LaSc$_2$N unit is planar, although earlier computations suggested that it would be pyramidal.



■ INTRODUCTION

The electric arc vaporization of a hollow graphite rod doped with a suitable metal oxide in a low-pressure helium atmosphere is the usual route for the preparation of endohedral fullerenes, closed cages of carbon atoms that encapsulate one or more metal atoms or a metal atom/main group clusters.[1,2] Unfortunately, these endohedral fullerenes are usually produced in rather low yields. However, incorporation of a source of nitrogen into the arc process produces new, more abundant families of metallic nitride fullerenes (MNFs) in which M$_3$N units are encapsulated in various sizes of fullerene cages.[3−6] Of these MNFs, M$_3$N@C$_{80}$ with an I_h fullerene cage is particularly prevalent, and significant improvements have been made in the separation and purification of this type of endohedral.[7,8]

It is also possible to prepare mixed-metal MNFs of the types MM′$_2$N@I_h-C$_{80}$ and MM′M″N@I_h-C$_{80}$ by suitable modification of the arc process of endohedral generation.[9,10] A number of such mixed-metal MNFs have been isolated and characterized, including ErSc$_2$N@I_h-C$_{80}$,[11] CeSc$_2$N@I_h-C$_{80}$,[12] GdSc$_2$N@I_h-C$_{80}$,[13,14] Gd$_2$ScN@I_h-C$_{80}$,[13,14] TbSc$_2$N@I_h-C$_{80}$,[13] YSc$_2$N@I_h-C$_{80}$,[15] and ErYScN@I_h-C$_{80}$.[16] Mixed-metal MNFs are in demand for fundamental science and for applications requiring entrapped clusters with dissimilar metals. Thus, the ErSc$_2$N rotor in ErSc$_2$N@I_h-C$_{80}$ may serve as a molecular memory element.[17] GdHoLuN@I_h-C$_{80}$ could have medical applications as a new type of multifunctional diagnostic agent, with uses for Gd in magnetic resonance imaging (MRI),[18−22] Ho in radiotherapy,[23] and Lu in X-ray contrast visualization.[24]

Difficulties in obtaining mixed-metal MNFs involve both poor yields in soot extracts and difficulties separating the mixed-metal MNFs from the more abundant empty-cage fullerene contaminants (C$_{60}$, C$_{70}$) and other MNF mixed-metal family members (e.g., A$_3$N@C$_{80}$, A$_2$ScN@C$_{80}$, ASc$_2$N@C$_{80}$, and Sc$_3$N@C$_{80}$, where A = transition or rare-earth metal). In this Article, we address both issues: the selective synthesis of mixed-metal MNFs and their separation. Promising results were recently obtained using the new CAPTEAR (chemically adjusting plasma temperature, energy, and reactivity) method for the selective synthesis of Sc$_3$N@C$_{80}$.[25,26] Here, we describe the use of CAPTEAR for synthesizing a mixed-metal rare-earth MNF. We also describe the use of a "stir and filter approach" (SAFA), to facilitate the separation of a mixed-metal MNF

Received: May 1, 2012
Published: December 6, 2012

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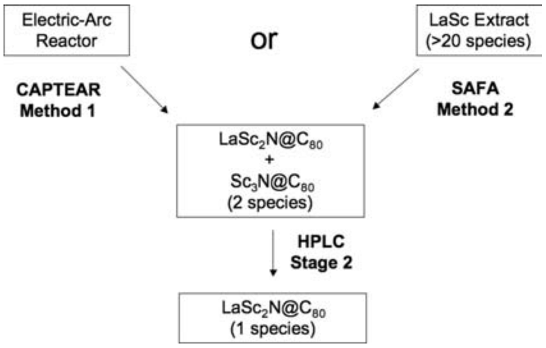
from raw fullerene soot.[27,28] The SAFA method uses amino-functionalized silica to selectively bind empty cage fullerenes and remove them from solution. This procedure has been shown to produce isomerically pure $Sc_3N@I_h\text{-}C_{80}$ from raw soot without the need for separation via HPLC.[28]

In the development of new synthesis and separation methods, we have focused on the incorporation of lanthanum into a mixed-metal MNF. Lanthanum is the largest of the lanthanide metals. Earlier work with lanthanum-containing MNFs revealed the formation of larger fullerene cages, particularly $La_3N@C_{88}$, $La_3N@C_{92}$, and $La_3N@C_{96}$, that seem best to accommodate this large ion, but provided no evidence for the existence of $La_3N@I_h\text{-}C_{80}$.[29] Additionally, computational studies suggest that $La_3N@I_h\text{-}C_{80}$ would be highly reactive.[30] In that context, it is surprising that $La_3N@C_{79}N$ has been detected.[31]

■ RESULTS AND DISCUSSION

Herein, we describe two approaches to isolate a mixed-metal MNF, as shown in Scheme 1. Method 1 uses as the synthetic process, the CAPTEAR approach to limit the number of different fullerenes and endohedral fullerenes formed by modification of the conditions of the electric arc synthesis. The alternative, method 2, consists of a bulk removal of non-MNF fullerenes (e.g., C_{60}, C_{70}) from arc-generated soot using SAFA to leave predominantly only two species in solution, the MNFs of $LaSc_2N@I_h\text{-}C_{80}$ and $Sc_3N@I_h\text{-}C_{80}$. These methods are complementary, not competitive. Stage 2 utilizes HPLC as a final cleanup step to separate and purify $LaSc_2N@I_h\text{-}C_{80}$.

Scheme 1. Integrated CAPTEAR-HPLC or SAFA-HPLC Approaches for Purifying $LaSc_2N@I_h\text{-}C_{80}$



Method 1: Selective Synthesis of Mixed-Metal $LaSc_2N@I_h\text{-}C_{80}$ via CAPTEAR. A mixture of metallic oxides (3:1 wt/wt, La_2O_3/Sc_2O_3) was packed in a cored graphite rod. No graphite powder was added to the mixture of metal oxides. This approach is dramatically different from other reports of MNF synthesis, in which graphite powder is present in a large excess of the metal content.[3,5,32] Our deviation from typical synthesis was done to enrich the percentage of MNFs in the fullerene extract.

The results for our experiments are shown in Figure 1, which shows MALDI-TOF mass spectra and HPLC chromatograms for the extract obtained from three different experiments. In the control experiment, no $Cu(NO_3)_2{\cdot}2.5H_2O$ was present, but in the subsequent experiments, 10 and 50 wt % $Cu(NO_3)_2{\cdot}2.5H_2O$ was added to the mixture of La_2O_3 and Sc_2O_3. As shown in parts (a) and (d) of Figure 1, $LaSc_2N@I_h\text{-}C_{80}$ forms along with $Sc_3N@I_h\text{-}C_{80}$, but there is no evidence for the formation of $La_2ScN@C_{80}$ or $La_3N@C_{80}$ in this study. The large size of lanthanium is likely to be the reason why these latter two endohedrals do not form. With only 10 wt % $Cu(NO_3)_2{\cdot}2.5H_2O$ added, there is more than an order of magnitude loss in the yield of C_{60}, which drops from 7.4 to 0.39 mg, as shown in Figure 1f. The yield of C_{70} drops a factor of 7 from 5.5 to 0.75 mg, as shown in Figure 1f. The ratio of $LaSc_2N@I_h\text{-}C_{80}$ to $Sc_3N@I_h\text{-}C_{80}$ appears to be comparable at 0, 10, and 50 wt % of added $Cu(NO_3)_2{\cdot}2.5H_2O$ (Figure 1a−e). The data in Figure 1f indicate that, with 50 wt % added $Cu(NO_3)_2{\cdot}2.5H_2O$, C_{60} and C_{70} are nearly absent in the soot extracts, but the yield of $LaSc_2N@I_h\text{-}C_{80}$ is also drastically reduced. On the basis of these results, a good compromise for making enriched soot extracts of $LaSc_2N@I_h\text{-}C_{80}$ would be on the order of 10 wt % of added $Cu(NO_3)_2{\cdot}2.5H_2O$ with the CAPTEAR synthesis.

Method 2: Selective Purification of $LaSc_2N@I_h\text{-}C_{80}$ via SAFA. Chloroform was selected as the solvent of choice for scale-up based on not only the rapid removal of empty-cage fullerenes (e.g., C_{60}, C_{70}, C_{78}, C_{84}) from solution but also, more importantly, that chloroform protected $LaSc_2N@I_h\text{-}C_{80}$ from uptake to diamino-functionalized silica, which was prepared as described previously.[8] As a demonstration of the scalability of SAFA separations with chloroform, 1000 mg of La/Sc-containing fullerene extract was dissolved in 10 L of chloroform by stirring the mixture overnight. The HPLC chromatogram for this solution is shown in Figure 2a. To this solution (which contained 0.1 mg of fullerene/mL) was added 400 g of dried diamino silica gel. Aliquots were taken periodically for monitoring the composition of fullerenes remaining in solution by HPLC. The reaction was stopped after 2.5 days, at which time there was no C_{60} and C_{70} observable in the HPLC chromatogram, as shown in Figure 2b.

From the 1000 mg of starting La/Sc-containing fullerene extract, ∼10 mg of a dried, fullerene mixture of $Sc_3N@I_h\text{-}C_{80}$ and $LaSc_2N@I_h\text{-}C_{80}$ was obtained after washing the isolated sample with diethyl ether and acetone and drying. This 10 mg sample was further separated by a single pass on the HPLC (Figure 2b), and a purified sample of $LaSc_2N@I_h\text{-}C_{80}$ was obtained (Figure 2c,d). Analysis of the purified sample by HPLC showed only $LaSc_2N@I_h\text{-}C_{80}$ when injected into an analytical PYE column at low flow rates of toluene mobile phase. HPLC, MALDI-TOF mass spectroscopy and subsequent X-ray crystallography confirm the identity of the isolated sample as isomerically purified $LaSc_2N@I_h\text{-}C_{80}$.

UV/vis Absorption Spectrum of $LaSc_2N@I_h\text{-}C_{80}$. A comparison of the UV/vis absorption spectra can now be made using isomerically purified samples of $Sc_3N@I_h\text{-}C_{80}$ and $LaSc_2N@I_h\text{-}C_{80}$ MNFs, as shown in Figure 3. Overall, there are similarities in the two electronic structures with minor differences. In $LaSc_2N@I_h\text{-}C_{80}$, there is a more pronounced peak around 740 nm relative to $Sc_3N@I_h\text{-}C_{80}$. The UV/vis spectra of other MNFs have been related to the structure of the cage (size and symmetry) as well as the charge on the cage.[9] The similarities in the UV/vis spectra (Figure 3) suggest that $Sc_3N@I_h\text{-}C_{80}$ and $LaSc_2N@I_h\text{-}C_{80}$ possess a similar cluster charge transfer and I_h cage structure.

Our UV/vis spectral results for $LaSc_2N@I_h\text{-}C_{80}$ and $Sc_3N@I_h\text{-}C_{80}$ are analogous to the findings of Dunsch et al.,[11,33] in which the UV/vis spectrum for their isolated, mixed-metal $GdSc_2N@I_h\text{-}C_{80}$ MNF had a more pronounced shoulder at ∼720 nm relative to $Sc_3N@I_h\text{-}C_{80}$. Wang *et al.*[10] also noticed a similarity in the UV/vis spectra of mixed-metal $CeSc_2N@I_h\text{-}C_{80}$

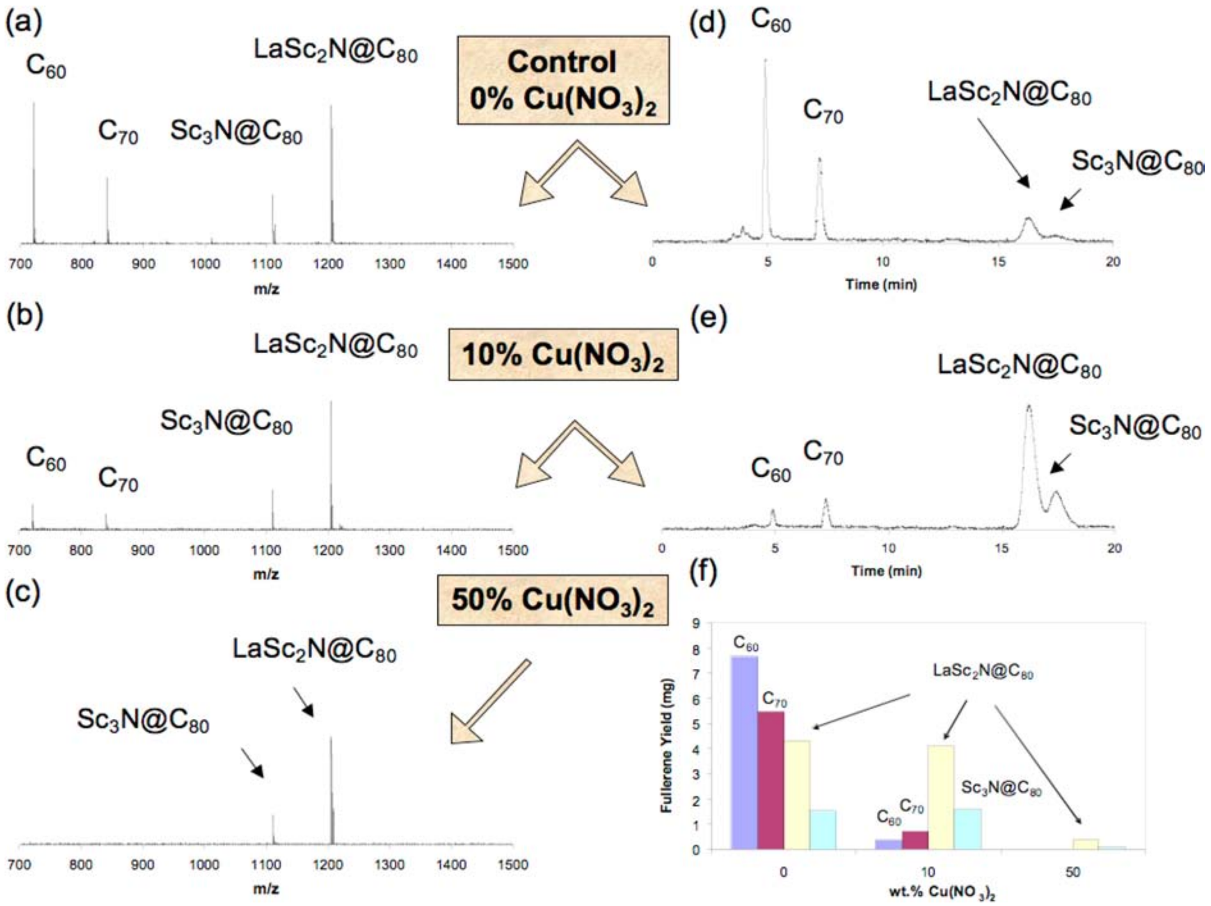


Figure 1. MALDI-TOF mass spectral (a−c) and HPLC (d,e) results for La-Sc fullerene extracts prepared from the electric-arc vaporization of packed rods containing various amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ added to a mixture of metal oxide powders containing a 3:1 ratio, wt/wt, of La_2O_3 to Sc_2O_3. The fullerene yield in milligrams is shown in (f).

and $Sc_3N@I_h$-C_{80} MNFs.[9] Chen et al. performed comparative UV/vis and reactivity studies with 1,3-dipolar cycloaddition for a complete set of $Y_3N@I_h$-C_{80}, $Y_2ScN@I_h$-C_{80}, $YSc_2N@I_h$-C_{80}, and $Sc_3N@I_h$-C_{80}, with the latter two MNFs possessing similar UV/vis spectra and reactivities.[34]

Structure of $LaSc_2N@I_h$-C_{80} from Single-Crystal X-ray Diffraction. Most fullerenes and endohedral metallofullerenes do not readily crystallize in an ordered fashion. The high symmetry of the exterior of the cages can facilitate cage disorder.[35−37] Additionally, there generally is a low barrier to movement of the metal ions within the cage,[38] and disorder in the position of the atoms or ions inside these cages can also occur. External functionalization has long been used to produce ordered fullerene cages[39] but has the potential to distort the cage geometry, particularly by opening C−C bonds in the cage.[40] Cocrystallization of endohedral fullerenes with Ni^{II}(OEP) (OEP is the dianion of octaethylporphyrin) is a useful method to form crystals with sufficient order for X-ray crystallography to yield structural information.[1,41] Suitable crystals were obtained by diffusion of a benzene solution of Ni^{II}(OEP) into a solution of $LaSc_2N@I_h$-C_{80} in benzene over a two-week period. Black crystals with the composition $LaSc_2N@I_h$-$C_{80} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$ were obtained and used for the X-ray diffraction study. Figure 4 shows a drawing of a $LaSc_2N@I_h$-C_{80} molecule and its relationship to the porphyrin.

As might be expected on the basis of ionic radii, the La−N distance (2.196(4) Å) in $LaSc_2N@I_h$-C_{80} is considerably longer than the Sc1−N and Sc2−N distances (1.943(6) and 1.921(7) Å, respectively). For comparison, the Sc−N distances are longer in related endohedrals: $Sc_3N@I_h$-C_{80}, 1.9931(14), 2.0323(16), and 2.0526(14) Å;[3] $Sc_3N@C_{78}$, 1.988(7), 1.983(15), and 2.125(5) Å;[42] and $Sc_3N@C_{68}$, 1.961(4), 1.974(4), and 2.022(3) Å,[43] despite the fact that the cage size is reduced in the last two cases. Thus, the presence of the large lanthanum ion acts to compress the two Sc−N bonds, but the $LaSc_2N$ unit remains planar. Similar considerations are seen in the structure of $CeSc_2N@I_h$-C_{80}, which contains a large cerium ion within the cage.[44] Within the $LaSc_2N$ unit, the Sc1−N−Sc2 angle is 116.88(19)° and the Sc1−N−La and Sc2−N−La angles are 121.5(3)° and 121.6(3)°, respectively. The sum of these three angles about the central nitrogen is 359.98°, and the $LaSc_2N$ unit is flat despite the need to accommodate the large lanthanum ion, as the view shown in Figure 5 demonstrates. Generally, M_3N units within fullerene cages are planar.[3,5,45] The extreme exception is the pyramidal Gd_3N unit in $Gd_3N@I_h$-C_{80}, where the nitrogen atom is displaced by 0.522(8) Å from the plane of the three gadolinium ions.[46] Additional examples of MNFs containing nonplanar M_3N units include $Tb_3N@I_h$-C_{80},[47] $Tb_3N@D_{5h}$-C_{80},[41] and an exohedral adduct of $Yb_3N@I_h$-C_{80}.[48] Previously, a computational study suggested that the nitrogen atom in $LaSc_2N@I_h$-C_{80} would protrude by 0.17 Å from the $LaSc_2$ plane.[30]

Figure 6 shows the locations of the metal ions relative to neighboring carbon atoms in the cage. The lanthanum ion lies near the center of a hexagon, while the two scandium ions are situated nearest the carbon atoms in 5:6 ring junctions.

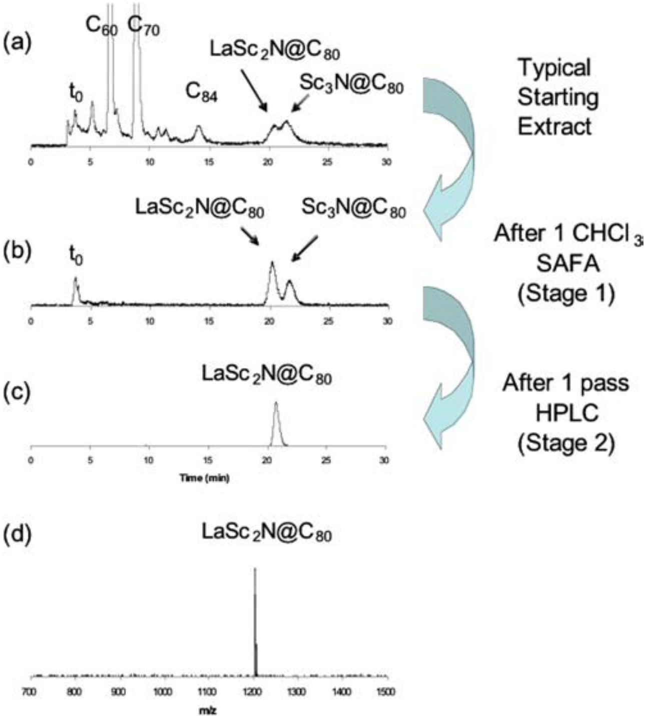


Figure 2. HPLC chromatograms of La-Sc extract at various stages of purification: (a) extract before purification, (b) after 1 SAFA-$CHCl_3$ enrichment step, and (c) after 1 HPLC pass, stage 2. The MALDI-TOF mass spectrum of purified $LaSc_2N@I_h$-C_{80} is shown in (d).

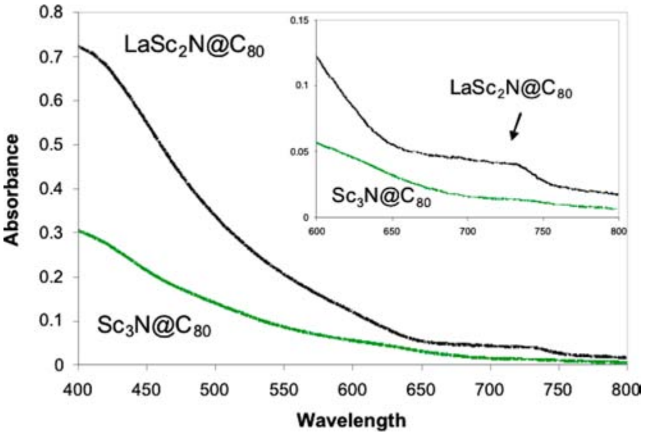


Figure 3. UV/vis spectra of purified samples of $LaSc_2N@I_h$-C_{80} and $Sc_3N@I_h$-C_{80} dissolved in carbon disulfide.

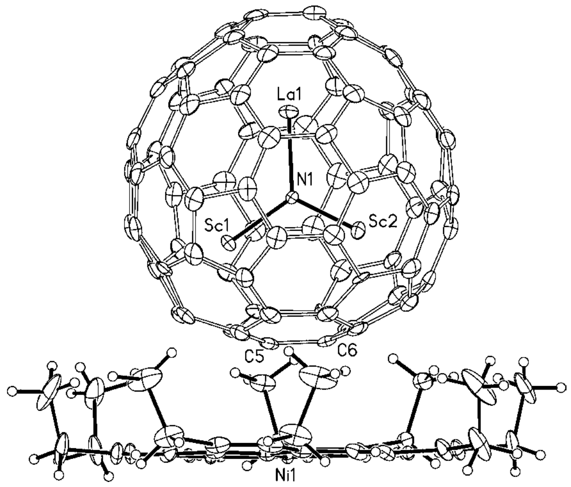


Figure 4. Perspective view of the relative orientations of $LaSc_2N@I_h$-C_{80} and $Ni^{II}(OEP)$ within crystalline $LaSc_2N@I_h$-$C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$. Thermal ellipsoids are shown at the 50% level.

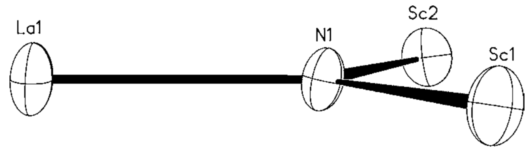


Figure 5. Edge-on view of the planar $LaSc_2N$ portion of $LaSc_2N@I_h$-$C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$ with 50% thermal contours.

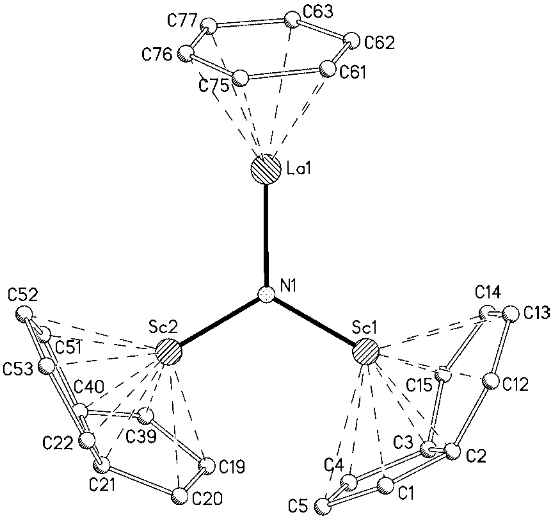


Figure 6. Position of the $LaSc_2N$ unit relative to the nearest carbon atoms of the I_h-C_{80} cage in $LaSc_2N@I_h$-$C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$. The La−C distances in the nearest six-membered ring range from 2.585(11) Å for La1−C77 to 2.629(6) Å for La1−C61. The shortest Sc−C distances are Sc1−C2, 2.220(7) Å, and Sc1−C3, 2.228(5) Å, for Sc1; and Sc2−C21, 2.197(7) Å, and Sc2−C40, 2.217(5) Å, for Sc2.

Inside the cage, the two scandium ions are situated near the metalloporphyrin, while the lanthanum ion is located on the far side of the cage, as seen in Figure 4. Figure 7A shows a view of the $LaSc_2N$ unit and its positioning relative to the plane of the $Ni^{II}(OEP)$ molecule. The $LaSc_2N$ unit is aligned nearly perpendicular to the plane of the porphyrin, and the scandium ions lie over a *trans* pair of porphyrin nitrogen atoms. Similar arrangements of the MSc_2N unit relative to the porphyrin plane are seen in cocrystals of $ErSc_2N@I_h$-C_{80} or $Sc_3N@I_h$-C_{80} with $Co^{II}(OEP)$ and cocrystals of $CeSc_2N@I_h$-C_{80}, $GdSc_2N@I_h$-C_{80}, or $TbSc_2N@I_h$-C_{80}, with $Ni^{II}(OEP)$.[13] There are also similarities among these cocrystals in their close contacts between the porphyrin and carbons of the C_{80} ball. In $LaSc_2N@I_h$-$C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$, the Ni1···C5 distance is 2.848(6) Å and the N3···C6 distance is 3.037(6) Å. Comparable distances are seen in the $Ni^{II}(OEP)$ cocrystals that encapsulate $TbSc_2N$, $GdSc_2N$, and $CeSc_2N$. The respective shortest Ni···C distances range from 2.835 to 2.855 Å, and the shortest N···C distances range from 3.044 to 3.072 Å. These close contacts are commonly ascribed to the effects of electrostatic attraction and $\pi\cdots\pi$ interactions.

To understand if the metal in the porphyrin was influencing the orientation of the $LaSc_2N$ unit, we also examined cocrystals of $LaSc_2N@I_h$-C_{80} with $H_2(OEP)$. Crystals of $LaSc_2N@I_h$-

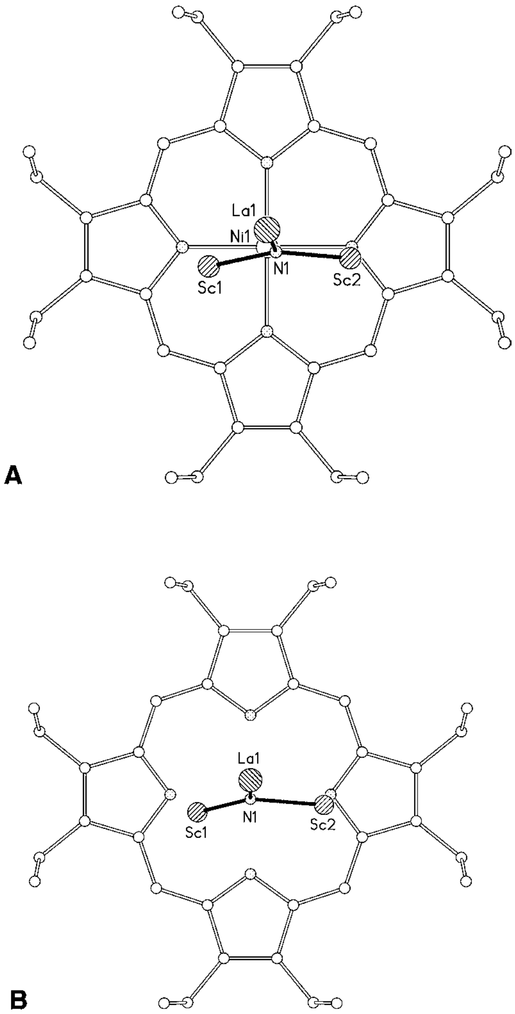


Figure 7. View of the $LaSc_2N$ unit with regard to the plane of the porphyrin from a vantage point perpendicular to the plane of the porphyrin: (A) $LaSc_2N@I_h\text{-}C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$ and (B) $LaSc_2N@I_h\text{-}C_{80}\cdot H_2(OEP)\cdot 2C_6H_6$. The positions of the hydrogen atoms are omitted.

$C_{80}\cdot H_2(OEP)\cdot 2C_6H_6$ are isostructural with crystals of $LaSc_2N@I_h\text{-}C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$. Consequently, the $LaSc_2N$ unit is aligned over the porphyrin in a similar fashion, as can be seen in Figure 7B. The nickel ion itself apparently does not play a key role in determining the positioning of the $LaSc_2N$ unit above the porphyrin.

■ CONCLUSIONS

Although HPLC has been the method of choice for separation and purification of fullerenes, metallofullerenes, and MNFs,[1,2,9] the HPLC approach has a number of drawbacks. In most soot extracts, there is the ubiquitous presence of not just C_{60} and C_{70} empty-cage fullerenes but also higher molecular weight empty-cage fullerenes and a variety of metallofullerenes and MNFs, which are coextracted from electric-arc soot. The dependence on HPLC methods for the entirety of a separation process is costly due to equipment, columns, solvent, and time, of which the latter can be overcome, in part, with automated HPLC systems.[49] For mixed-metal soot extracts, the product distribution is even more complex with added mixed-metal metallofullerenes being present in addition to homometallic endohedrals. Overall, there is a need for a new separation method and/or a new selective synthesis approach to decrease the types of fullerenes made in the electric-arc reactor.

The results reported here indicate that mixed-metal, soot extract produced via the CAPTEAR method with $Cu(NO_3)_2\cdot 2.5H_2O$ is enriched in MNFs and depleted of empty-cage fullerenes, thereby alleviating the burden of removing C_{60}, C_{70}, and higher empty-cage fullerenes. Alternatively, the SAFA method can be used to remove the empty cage fullerenes from a carbon soot sample prepared without using $Cu(NO_3)_2\cdot 2.5H_2O$.

$LaSc_2N@I_h\text{-}C_{80}$ has been characterized by UV/vis absorption spectroscopy and by single-crystal X-ray diffraction. Similarly ordered crystals have been obtained by cocrystallization of $LaSc_2N@I_h\text{-}C_{80}$ with either $Ni^{II}(OEP)$ or $H_2(OEP)$.

■ EXPERIMENTAL SECTION

Electric-Arc Synthesis of $LaSc_2N@I_h\text{-}C_{80}$. Our vaporization process has been previously described and involves the core-drilling of 1 in. diameter graphite rods (Carbone of America) from 6 to 4 in., a length of a cored rod corresponding to 30 g of carbon in the outer shell.[25,50] These rods were then packed with a 3:1 wt/wt ratio of La_2O_3 and Sc_2O_3 powders (Stanford Materials) to which a mixture of $Cu(NO_3)_2\cdot 2.5H_2O$ (Sigma-Aldrich) could be added. Additional reactor parameters were 250 A, gap voltage of 37 V, and 400 Torr He under dynamic flow. An airflow of 4 Torr/min was added to the reactor. Under these conditions, typical times to vaporize the 4 in. segment of packed rods were 45−60 min. The harvested soot from the reactor was extracted with *o*-xylene, filtered, dried, and washed with ether and acetone. Extracts were characterized by HPLC and MALDI-TOF mass spectrometry.

Large-Scale SAFA Separations of La-Sc Fullerene Extracts. The La-Sc extract obtained from the vaporization of 20 rods under CAPTEAR and control conditions were combined to obtain 1 g of fullerene material. Diamino-functionalized silica gel was prepared from unfunctionalized silica gel purchased from Sigma-Aldrich with the following specifications: BET surface area of approximately 500 m^2/g, pore volume 0.75 cm^3/g, 70−270 mesh, and 60 Å (for column chromatography). The diamino-functionalized silica was prepared and utilized under the conditions specified in ref 8.

The large-scale isolation of $LaSc_2N@I_h\text{-}C_{80}$ using SAFA was conducted with chloroform (ACS grade from Sigma-Aldrich). In this experiment, 1000 mg of La-Sc fullerene extract was dissolved in 10 L of chloroform. To this solution of 0.1 mg fullerene/mL was added 400 g of diamino silica, which was dried for 2 h in a vacuum oven at 80 °C and cooled for 4.5 h. The vacuum oven was repressurized with N_2, and the diamino silica was immediately added to the extract solution. As the slurry was stirred, aliquots of the reaction mixture were injected into an HPLC column, (PYE stationary phase, 4.6 × 250 mm, Phenomenex) for analysis of fullerenes remaining in solution. Chromatographic conditions for analytical separations of timed aliquots were the following: a flow rate of 1 mL/min, *o*-xylene as the mobile phase, PYE column, 360 nm UV detection, and 50 μL injection volumes. The stirring for this large-scale SAFA experiment continued for 2.5 days with periodic monitoring of fullerene uptake to determine when C_{60} and C_{70} levels in our aliquots fell below the detection limits of our HPLC. From the 1000 mg of starting La-Sc fullerene extract, 100 mg of sample was obtained after solvent removal. Upon washing with diethyl ether and acetone, ~10 mg of a dried, fullerene mixture of $Sc_3N@I_h\text{-}C_{80}$ and $LaSc_2N@I_h\text{-}C_{80}$ was obtained. Upon a single HPLC pass (Figure 2c) with a 10 mm × 250 mm PYE column (Phenomenex), a purified sample of $LaSc_2N@I_h\text{-}C_{80}$ was obtained.

Cocrystallization of $LaSc_2N@I_h\text{-}C_{80}$. Cocrystals of $LaSc_2N@I_h\text{-}C_{80}$ with either $Ni^{II}(OEP)$ or $H_2(OEP)$ were obtained by layering a red benzene solution of $Ni^{II}(OEP)$ or $H_2(OEP)$ over a brown solution of the endohedral in benzene in a glass tube. Over a period of several weeks, the two solutions diffused together and black crystals formed.

X-ray Crystallography and Data Collection. The crystals were removed from the glass tubes in which they were grown together with a small amount of mother liquor and immediately coated with hydrocarbon oil on the microscope slide. A suitable crystal of $LaSc_2N@I_h\text{-}C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$ was mounted on a glass fiber with silicone grease and placed in the 90(2) K dinitrogen stream supplied by a Cryo Industries CRYOCOOL device. Diffraction data were collected with a Bruker ApexII diffractometer with graphite-monochromated Mo Kα radiation. Data for the $H_2(OEP)$ cocrystal were obtained with the use of synchrotron radiation at the Advanced Light source with radiation having a wavelength of 0.7749 Å and a similar diffractometer. The low-temperature apparatus was an Oxford model. The structures were solved by direct methods and refined using all data (based on F^2) using the software of SHELXTL 5.1.[51] In both structures the C_{80} and two Sc's are disordered with respect to a crystallographic mirror plane, and therefore, these atoms were refined with symmetry removed (PART-1) at half-occupancy. All non-hydrogen atoms were assigned anisotropic displacement parameters. Because of the propensity of fullerene cages to show some rotational motion, the carbons of the C_{80} were restrained with use of an ISOR 0.008 command.

$LaSc_2N@I_h\text{-}C_{80}\cdot Ni^{II}(OEP)\cdot 2C_6H_6$: $C_{128}H_{56}N_5LaNiSc_2$, M = 1951.32; black block; 0.14 mm × 0.10 mm × 0.08 mm; monoclinic; $C2/m$; a = 25.3518(8) Å, b = 14.9702(8) Å, c = 19.6995(8) Å; β = 95.385(4)°; Mo Kα, λ = 0.71073 Å; T = 90(2) K; V = 7443.4(6) Å^3; Z = 4; 47 355 reflections measured, 10 382 unique (R_{int} = 0.0521); 2θ max = 58.23°; min/max transmission = 0.87/0.92; final wR(F^2) = 0.1085 (all data), conventional R1 = 0.0400 computed for 1010 parameters with 480 restraints.

$LaSc_2N@I_h\text{-}C_{80}\cdot H_2(OEP)\cdot 2C_6H_6\cdot 0.06Ag$: $C_{128}H_{58}N_5LaSc_2$, M = 1899.08; black parallelepiped; 0.05 mm × 0.02 mm × 0.01 mm; monoclinic; $C2/m$; a = 25.2727(15) Å, b = 15.027(2) Å, c = 19.664(2) Å; β = 94.970(6)°; synchrotron radiation, λ = 0.77490 Å; T = 100(2) K; V = 7439.7(14) Å^3; Z = 4; 70 462 reflections measured, 13 554 unique (R_{int} = 0.0406); 2θ max = 71.16°; min/max transmission = 0.96/0.99; final wR(F^2) = 0.2191 (all data), conventional R1 = 0.0691 computed for 1005 parameters with 480 restraints. In addition, the displacement parameters of two nearby carbons of the $H_2(OEP)$ cocrystal were restrained to be equal (EADP command). A minor second La position in the structure of the $H_2(OEP)$ cocrystal was included; refined occupancies were 0.4779(5):0.0221(5). The structure contains a small defect electron density that shows up as 9 e$^-$/Å^3 in the difference map. The nature of this defect is unknown. It is close to the position that could be occupied by a transition metal bonded to the OEP of the porphyrin, but is not symmetrically located in the porphyrin plane. It was arbitrarily assigned as Ag since the glassware could have had this contamination. The occupancy of Ag1, which is located on the crystallographic mirror plane, was refined to 0.0303(9).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the U.S. National Science Foundation (Grants CHE-1011760 to A.L.B. and M.M.O., CHE-0547988 to S.S.), the DOE GAANN Fellowship (P200A060323 to S.S.), and the Advanced Light Source, Lawrence Berkeley Laboratory, for support. The Advanced Light Source is funded by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

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