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Isolation of $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ through a Non-Chromatographic, Two-Step Chemical Process and Crystallographic Characterization of the Pyramidalized CeLu_2N within the Icosahedral CageSteven Stevenson,^{*,[a]} Hannah R. Thompson,^[a] Kristine D. Arvola,^[a] Kamran B. Ghiassi,^[b] Marilyn M. Olmstead,^{*,[b]} and Alan L. Balch^{*,[b]}

Abstract: By combining two chemical methods of purification, 4 mg of purified $\text{CeLu}_2\text{N}@C_{80}$ was readily isolated from 500 mg of carbon soot extract without the use of recycling HPLC, a method which has previously been necessary to obtain pure samples of endohedral fullerenes. In stage 1, $\text{CeLu}_2\text{N}@C_{80}$ was selectively precipitated by virtue of its low first oxidation potential (+0.01 V) and the judicious choice of MgCl_2 as the Lewis acid precipitant. For stage 2, we used

a stir and filter approach (SAFA), which employed the electron-rich NH_2 groups immobilized on silica gel to selectively bind residual endohedrals and higher cage fullerenes that were contaminants from stage 1. Crystallographic analysis of $\text{CeLu}_2\text{N}@C_{80}$ in the co-crystal $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}\cdot\text{Ni}(\text{octaethylporphyrin})\cdot 2(\text{toluene})$ reveals that the $I_h\text{-C}_{80}$ cage is present with a pyramidalized CeLu_2N unit inside.

Introduction

Numerous trimetallic nitride endohedral fullerenes ($\text{M}_3\text{N}@C_{2n}$ with $2n$ in the range 68–88) have been isolated and purified from carbon soot prepared using metal-oxide-doped graphite rods in an electric arc fullerene generator.^[1–27] Purification of these materials requires separation of cages of different sizes and, for a given cage size, separation of cage isomers. In addition, it is also possible to isolate and purify mixed-metal species, $\text{MM}_2'\text{N}@C_{2n}$.^[28–50] Here, there is an added degree of complexity to the isolation process: the separation process must be responsive to the contents *inside* the cage. Finally, it has been possible to purify an endohedral fullerene containing three different metal ions: $\text{ScYErN}@C_{80}$.^[51]

Endohedral fullerenes of the types $\text{M}_3\text{N}@C_{2n}$ and $\text{MM}_2'\text{N}@C_{2n}$ have remarkable properties that make them promising for several applications. Gadolinium-containing endohedral fullerenes are effective relaxation agents for magnetic resonance imaging (MRI).^[2] The incorporation of a second metal ion into such a molecule allows dual function. For example, $\text{GdLu}_2\text{N}@C_{80}$ and $\text{HoLu}_2\text{N}@C_{80}$ have been proposed as multi-functional agents for simultaneous use in MRI (Gd) with X-ray contrast (Lu) or radiopharmaceutical (Ho) with X-ray contrast (Lu), respectively.^[52]

The incorporation of paramagnetic rare-earth metal ions into mixed-metal endohedrals (e.g., $\text{HoSc}_2\text{N}@C_{80}$,^[53] $\text{DySc}_2\text{N}@C_{80}$,^[54]) generates new magnetic materials. The redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple in the mixed-metal endohedrals $\text{CeSc}_2\text{N}@C_{80}$, $\text{CeY}_2\text{N}@C_{80}$, and $\text{CeLu}_2\text{N}@C_{80}$ varies in response to the different metal ions within the cage.^[34,35,40,43,55] Finally, the mixed-metal endohedral $\text{LaSc}_2\text{N}@C_5(\text{hept})\text{-C}_{80}$ is the first and only example of an endohedral fullerene that contains a heptagon as a part of the cage.^[56] All other endohedral fullerenes have cages made up of twelve pentagons and a number of hexagons, with the latter determined by the cage size.

The arc synthesis of mixed-metal nitride endohedrals is more facile than their purification. Their low abundance in soot extract represents another challenge in their isolation. For example, $\text{CeLu}_2\text{N}@C_{80}$ is typically present at <1% in the soot extract prepared under a He/N_2 atmosphere. The remaining 99+ % of soluble species contains mostly lower empty-cage (e.g., C_{60} , C_{70}) and higher empty-cage fullerenes (e.g., C_{84} – C_{140}), along with smaller amounts of monometallic ($\text{A}@C_{2n}$, $n=30$ –46), dimetallic ($\text{A}_2@C_{2n}$, $\text{AB}@C_{2n}$), and trimetallic endohedrals.

HPLC, which has been used to purify most mixed-metal nitride endohedrals, has drawbacks that include a high cost of proprietary columns, requirement of a stationary phase capable of resolving cages with similar clusters, long retention times required for resolution of closely eluting species, and large volumes of mobile phase, which must later be removed from the collected fractions. Multiple types of specialty columns (e.g., PYE, BuckyPrep-M, BuckyPrep, PBB, Buckyclutcher) are used, and often in conjunction with recycling HPLC.

Examples of mixed-metal nitride endohedrals and their recycling HPLC times include $\text{LuSc}_2\text{N}@C_{68}$ (400 min),^[57] $\text{DySc}_2\text{N}@C_{76}$ (300 min),^[58] and $\text{TiSc}_2\text{N}@C_{80}$ (100 min).^[59] Typical resolution

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times from recycling HPLC range from 100–400 min. Extreme examples of very lengthy separation times for the recycling HPLC method were 2900 min to resolve and remove $Y_3N@D_{5h}-C_{80}$ from $CeY_2N@I_h-C_{80}$ species^[40] and 4280 min to separate $CeY_2N@C_{84}$ from $Y_3N@C_{84}$.^[43]

Empty-cage fullerenes have been shown to precipitate in the presence of Lewis acids (LA).^[60–63] In a chemical-based separation method for empty-cage fullerenes, $AlCl_3$ was used to purify C_{60} from C_{70} .^[63] Subsequently, Lewis acids such as $FeCl_3$, $AlCl_3$, and $AlBr_3$ were added to metallofullerene mixtures to selectively precipitate the endohedrals from the empty-cage fullerenes in soot extracts.^[64] Shortly thereafter, a different Lewis acid, $TiCl_4$, was also successful in selectively reacting with mono- and dimetal, and dimetal carbide endohedrals.^[65,66] Although several Lewis acids and solvents were investigated, the best recovery of endohedrals from their Lewis acid complexes was found when $TiCl_4$ was used.^[66] A correlation between the first oxidation potential of a metallofullerene and its reactivity threshold with a Lewis acid has been reported, and a mechanism has been proposed.^[65,66] $TiCl_4$ is also useful to selectively complex and isolate the missing small-bandgap metallofullerenes, $(Y@C_{2n}-(CF_3)_m)$ as their trifluoromethyl derivatives.^[67]

More recently, other Lewis acids have been investigated. For example, $CuCl_2$ could selectively precipitate metallic oxide fullerenes, metallic nitride fullerenes, and separate two structural isomers for $Er_2@C_{82}$.^[68] For the MRI-active Gd-based metal nitride species, the reactivity of $Gd_3N@C_{78-92}$ with eleven Lewis acids ($CaCl_2 < ZnCl_2 < NiCl_2 < MgCl_2 < MnCl_2 < CuCl_2 < WCl_4 \ll WCl_6 < ZrCl_4 < AlCl_3 < FeCl_3$) was investigated.^[69] $CaCl_2$, $ZnCl_2$, and $NiCl_2$ were the most selective and had the lowest precipitation thresholds ($< +0.19$ V). Intermediate precipitation thresholds (i.e., between $+0.19$ – 0.4 V) were found for $MgCl_2$, $MnCl_2$, $CuCl_2$, and WCl_4 .^[69] The lowest selectivity for individual metallofullerenes was achieved with the most reactive Lewis acids (WCl_6 , $ZrCl_4$, $AlCl_3$, and $FeCl_3$), which had the highest precipitation onsets ($> +0.5$ V). With this broad spectrum of Lewis acid strengths, it was possible to control which metallic nitride fullerenes would remain in solution and which endohedrals would precipitate. In this manner, an enriched sample of $Gd_3N@C_{88}$ was obtained with $ZnCl_2$.^[69]

It is known that empty-cage fullerenes will react with aliphatic amines.^[70] Placing the electron-rich $-NH_2$ group onto a solid support (i.e., aminosilica) is a useful way to immobilize and remove empty-cage fullerenes and contaminant endohedrals from solution.^[47,71–74] As an example, dried aminosilica has been added to solutions of La/Sc soot extract. After filtering the reaction slurry, the filtrate contained predominantly two endohedrals, $Sc_3N@I_h-C_{80}$ and $LaSc_2N@I_h-C_{80}$, which were the most inert to aminosilica and remained in solution.^[47] This stir and filter approach (SAFA) has also been used to purify homometallic $M_3N@I_h-C_{80}$ cages, such as $Sc_3N@I_h-C_{80}$ ^[73,74] and $Er_3N@I_h-C_{80}$.^[71] Other methods to non-chromatographically separate metallic nitride fullerenes include selective chemical oxidation,^[75,76] Diels–Alder reactions,^[77,78] and complexation.^[79]

In this work, we describe a method that avoids recycling HPLC and eliminates chromatography as a means of isolating a mixed-metal species.

Results and Discussion

We hypothesized that no two endohedrals would have exactly the same reactivity toward an electron-poor Lewis acid such as $MgCl_2$ and toward an electron-rich aminosilica gel, which is the reactive support used in SAFA. This new LA–SAFA separation method is based on a dual selectivity approach. By combining the selectivity of Lewis acid fractionation (stage 1) with the “survival of the most inert” endohedral in the SAFA process (stage 2), we have isolated the first mixed-metal $CeLu_2N@I_h-C_{80}$ endohedral by a non-chromatographic approach. An overview of the LA–SAFA separation method is shown in Scheme 1.

Scheme 1. The LA–SAFA separation method for $CeLu_2N@I_h-C_{80}$.

Enrichment of $CeLu_2N@C_{80}$ by precipitation with $MgCl_2$ (stage 1)

Carbon soot was obtained by vaporization of cored graphite rods containing a mixture of Lu_2O_3 and CeO_2 in an electric-arc reactor under a low pressure He/N_2 atmosphere. After extraction with carbon disulfide and evaporation, a portion of dry Ce/Lu-based soot extract (500 mg) was dissolved into carbon disulfide (500 mL). The MALDI mass spectrum of the raw Ce/Lu extract is shown in Figure 1a. Analysis of the MALDI data reveals the presence of more than 100 different types of fullerenes and metallofullerenes. The compounds present in this mixture include: empty-cage fullerenes (e.g., C_{2n} , which are the dominant species), homometallic endohedrals (e.g., $Ce@C_{2n}$, $Ce_2@C_{2n}$, $Lu@C_{2n}$, $Lu_2@C_{2n}$), homotrimetallic nitride metallofullerenes ($Lu_3N@C_{2n}$), and the desired mixed-metal nitride endohedrals ($Ce_xLu_{3-x}N@C_{2n}$ in which $x=1, 2$), which were present at $< 1\%$ abundance.

For round 1 of the purification process of stage 1, anhydrous $MgCl_2$ (1.87 g) was added to the Ce/Lu soot extract. After 19 h, the reaction mixture was filtered to obtain a sample of precipitated endohedrals. Upon decomplexation of the endohedral fullerenes by treating the precipitated material with a mixture of ice and carbon disulfide, there are three dominant endohedrals ($Ce@C_{82}$, $Ce_2LuN@C_{80}$ and $CeLu_2N@C_{80}$) as shown in the mass spectral data in Figure 1b.

To assess whether further selectivity could be achieved, in round 2 an additional portion of anhydrous $MgCl_2$ (5.6 g) was added to the filtrate remaining after round 1 and the reaction was allowed to proceed for 26 h. Further precipitation occurred, and mass spectral analysis (Figure 1c) of the endohedrals obtained after decomplexation of the precipitate indicat-

Figure 2. HPLC of a) Ce/Lu raw soot extract, b) enriched $\text{CeLu}_2\text{N@C}_{80}$ obtained after round 2 of MgCl_2 treatment (see Figure 1c), c) purified $\text{CeLu}_2\text{N@C}_{80}$ obtained after 2 days of SAFA reaction and d) corresponding MALDI mass spectrum) round 3.

ed a highly enriched sample of the targeted $\text{CeLu}_2\text{N@C}_{80}$, which is clearly the dominant species at 85% purity.

Because the majority of the endohedrals were not yet precipitated, additional anhydrous MgCl_2 (7.5 g) was added to the filtrate that remained after round 2. After an increased reaction time (2 d), further complexation occurred to produce a round 3 precipitate. Upon decomplexation and subsequent analysis by mass spectrometry, the round 3 precipitate contained five dominant peaks as shown in Figure 1d. In addition to residual $\text{CeLu}_2\text{N@C}_{80}$, this precipitate contained $\text{Ce}_2\text{@C}_{72}$, Lu_2C_{84} , and two mixed-metal nitride endohedrals, $\text{Ce}_2\text{LuN@C}_{88}$ and $\text{CeLu}_2\text{N@C}_{88}$.

The unreactive fullerenes and endohedrals that survived all three rounds of precipitation with MgCl_2 remained in the filtrate from round 3. The mass spectrum of this solution shows two dominant endohedral peaks due to $\text{Lu}_2\text{@C}_{82}$ and $\text{Lu}_3\text{N@C}_{80}$ and many empty cage fullerenes. The remaining MALDI peaks correspond primarily to the more unreactive empty-cage fullerenes. A summary of the results from Lewis acid treatment is given in Table 1.

Isolation of $\text{CeLu}_2\text{N@C}_{80}$ with SAFA (stage 2)

Comparing the MALDI data in Figure 1, the Lewis acid obtained fraction that is closest to purification is

the highly enriched $\text{CeLu}_2\text{N@C}_{80}$ sample obtained in the round 2 precipitate (see Figure 1c). For this reason, the sample from the round 2 precipitate was selected for the stage 2 treatment with aminosilica using SAFA. The goal for stage 2 was incorporating a different class of reaction to achieve even further selectivity for endohedral separations.

An enriched $\text{CeLu}_2\text{N@C}_{80}$ sample (10 mg) corresponding to the trace shown in Figure 1c was dissolved in xylenes (135 mL). The HPLC data shown in Figure 2a and 2b demonstrate the effectiveness of the stage 1 (Lewis acid, MgCl_2) pre-cleanup of $\text{CeLu}_2\text{N@C}_{80}$ from the Ce/Lu soot extract. Freshly vacuum-dried aminosilica gel was immediately added to this $\text{CeLu}_2\text{N@C}_{80}$ enriched sample with stirring. Aliquots from this reaction mixture were analyzed by HPLC to determine when to stop the reaction. When the contaminant peaks from other fullerene species were removed (48 h), the reaction slurry was filtered. HPLC analysis of the filtrate obtained after the SAFA reaction, as

Figure 1. MALDI mass spectra for a) raw Ce/Lu soot extract, decomplexed endohedrals from precipitates after b) round 1 MgCl_2 , c) round 2 MgCl_2 , d) round 3 MgCl_2 , and e) unreactive fullerenes and metallofullerenes remaining in the filtrate.

Table 1. Products of selective precipitation using MgCl_2 .

Separation stage	Dominant endohedrals present
round 1 precipitate	Ce@C_{82} , $\text{Ce}_2\text{LuN@C}_{80}$
round 2 precipitate	$\text{CeLu}_2\text{N@C}_{80}$
round 3 precipitate	$\text{Ce}_2\text{@C}_{72}$, Lu_2C_{84} , $\text{Ce}_2\text{LuN@C}_{88}$, $\text{CeLu}_2\text{N@C}_{88}$
round 3 filtrate (inert)	$\text{Lu}_2\text{@C}_{82}$, $\text{Lu}_3\text{N@C}_{80}$, C_{60} , C_{70} , larger empty-cage fullerenes

shown in Figure 2c, demonstrates that $\text{CeLu}_2\text{N}@C_{80}$ is isolated in 95% purity. The corresponding MALDI mass spectrum of the SAFA filtrate, after solvent removal and washing with diethyl ether, shown in Figure 2d, also confirms the high purity of the sample.

Although not the focus of this $\text{CeLu}_2\text{N}@C_{80}$ work, the enriched endohedrals shown in Scheme 2, may also, in principle, be isolated by implementing the LA–SAFA approach discussed

Scheme 2. Selective fractionation and metallofullerene enrichment

herein. For example, $\text{Ce}_2\text{LuN}@C_{80}$, enriched and located in the decomplexed round 1 precipitate of stage 1, should be amenable toward further purification by adding the SAFA component to complete the LA–SAFA method. Likewise, the dominant endohedrals from the round 3 precipitate of stage 1, for example, $\text{Ce}_2@C_{72}$, $\text{CeLu}_2\text{N}@C_{88}$, and $\text{Ce}_2\text{LuN}@C_{88}$, may also be further enriched or purified by adding the selectivity of a SAFA step.

X-ray crystallographic characterization of $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$

Crystals were obtained by diffusion of a solution of $[\text{Ni}^{\text{II}}(\text{OEP})]$ (OEP = octaethylporphyrin) in toluene into a solution of $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ in toluene over a two-week period.^[80] Black crystals of $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_7\text{H}_8$ formed, and these were used for the single-crystal X-ray diffraction study. Figure 3 shows the structure of $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$, itself. This drawing shows the position of the fully ordered $I_h\text{-C}_{80}$ cage and the major location of the CeLu_2N unit, which has 0.65 fractional occupancy. There are two positions for the nitrogen atom with occupancies of 0.53/0.47 for N1A/N1B. N1A is displaced 0.349(8) Å out of the least-squares plane of Ce1/Lu1/Lu2 (the major form), while N1B is displaced $-0.325(8)$ Å away from the same plane. Thus, the CeLu_2N unit is pyramidalized. In addition, there are other positions for the metal atoms within the cage: seven for Lu, four for Ce.

The cluster geometry can be compared to the known structures of $\text{CeSc}_2\text{N}@I_h\text{-C}_{80}$ ^[48] and $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$.^[11] In $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$, the Lu–N distances range from 1.980(6) to 2.0819(8) Å and the Lu_3N unit is planar.^[11] The Lu–N distances in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ fall in this range. Figure 4 compares some structural parameters for the pyramidal CeLu_2N unit in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ and the planar CeSc_2N unit in $\text{CeSc}_2\text{N}@I_h\text{-C}_{80}$.^[48] As expected the Lu–N distances

Figure 3. The structure of the $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ molecule in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_7\text{H}_8$. Only the location of the major site of the CeLu_2N unit with the metals at 65% occupancy is shown along with the two positions of the nitrogen atom.

Figure 4. Comparison of the structures of the pyramidal CeLu_2N unit in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ with the planar CeSc_2N unit in $\text{CeSc}_2\text{N}@I_h\text{-C}_{80}$. Only one of the two nitrogen atoms was used to produce the figure on the left. Similar distances and angles are found for the other nitrogen site.

ces are longer than the Sc–N distances, but the Ce–N distance in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ is shorter than the Ce–N distance in $\text{CeSc}_2\text{N}@I_h\text{-C}_{80}$. This shortening must arise from the constraints of placing larger atoms within the confines of an $I_h\text{-C}_{80}$ cage. These constraints also produce the pyramidal shape of the CeSc_2N cluster. It is revealing that the Ce site has longer distances to the interior of the cage than either of the Lu sites. All three metals reside under hexagons, but are slightly shifted from the hexagon center towards a nearby 5:6 junction. The average of the nearest six M–C distances is 2.560 Å for the Ce site, and 2.384, 2.402 Å for the two Lu sites.

The pyramidalization of the CeLu_2N unit in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$ is surprising. Generally, M_3N units are planar over a variety of cage sizes. For example, in the series $\text{Gd}_3\text{N}@C_{2n}$ ($2n = 76, 80, 82, 84, 86$ and probably for 88 as well) the Gd_3N unit is planar except for $\text{Gd}_3\text{N}@C_{80}$.^[2] In $\text{Gd}_3\text{N}@C_{80}$, the nitrogen atom is disordered in the same fashion as seen here in $\text{CeLu}_2\text{N}@I_h\text{-C}_{80}$.^[28] N1A in $\text{Gd}_3\text{N}@I_h\text{-C}_{80}$ is 0.522(8) Å away from the Gd_3 plane, while N1B is 0.463 Å out of the Gd_3 plane on the other side. The Tb_3N units in $\text{Tb}_3\text{N}@I_h\text{-C}_{80}$ and $\text{Tb}_3\text{N}@D_{5h}\text{-C}_{80}$ are also pyramidalized.^[15] In $\text{Tb}_3\text{N}@I_h\text{-C}_{80}$, N1A is $-0.453(4)$ Å away from the

Tb₃ plane, while N1B is 0.405(7) Å from that plane. In Tb₃N@D_{5h}-C₈₀, the nitrogen to Tb₃ plane distance is 0.505(14) Å. The Y₃N unit in Y₃N@C₈₀ is also slightly pyramidalized with the nitrogen atom 0.13 Å out of the Y₃ plane.^[81] Previously, DFT computations on CeLu₂N@I_h-C₈₀ had predicted that the cluster would be planar.^[34,40] The sizes of the encapsulated metal ions and the rigid nature of the I_h-C₈₀ cage are responsible for the pyramidal nature of this CeLu₂N unit.

As the top part of Figure 5 shows, the fullerene is positioned within the arms of the nickel octaethylporphyrin complex in a manner that has often been observed.^[1,80,82] The bottom part of Figure 5 shows a location of the CeLu₂N unit relative to the plane of the [Ni(OEP)] molecule. The two lutetium atoms reside near the nitrogen atoms of the porphyrin, with the unique cerium atom positioned furthest from that plane. This orientation of the CeLu₂N unit is similar to that seen in many

other crystal structures of cocrystals of [Ni(OEP)] and M₃N@I_h-C₈₀.^[48,82]

Conclusion

We have isolated a mixed-metal nitride endohedral, CeLu₂N@I_h-C₈₀, without using HPLC or recycling HPLC for its purification. The CeLu₂N@I_h-C₈₀ purification was done by using a dual mode, chemical attack with a Lewis acid (electron-poor) in stage 1 coupled with a different reaction type (electron-rich) with immobilized amines in a SAFA step (stage 2). This new LA-SAFA approach used readily available materials and produced the isolated sample that was characterized by X-ray crystallography. The structure of CeLu₂N@I_h-C₈₀ in CeLu₂N@I_h-C₈₀·Ni(OEP)·2C₇H₈ shows the presence of an ordered I_h-C₈₀ cage with a pyramidalized CeLu₂N cluster inside.

Experimental Section

Soot extract and fractionation with MgCl₂ (stage 1)

To prepare Ce/Lu endohedral soot extract, a mixture of Lu₂O₃ (200 g) and CeO₂ (300 g) was packed into cored graphite rods and vaporized in an electric-arc reactor containing a He/N₂ atmosphere. The metallofullerene synthesis and extraction was previously described.^[1,83] A portion of Ce/Lu soot extract (500 mg) was added to a round bottom flask containing carbon disulfide (500 mL) and soaked for 4 h. The extract solution was filtered using a PTFE membrane, and the filtrate was transferred to a 1 L round bottom flask. While vigorously stirring, anhydrous MgCl₂ powder (1.87 g, freshly opened) was added, and the reaction proceeded for 19 h. After Buchner filtration of the reaction mixture, the wet, solid material collected on the filter paper was washed with CS₂ (50 mL) and immediately added to a 1 L beaker containing a mixture (50:50, v/v) of ice chunks and CS₂. After 4 h of stirring, decomplexation and recovery of endohedrals was achieved, and the metallofullerenes were transferred to the lower CS₂ layer. After multiple washings with water in a separatory funnel, the CS₂ layer was transferred to a round-bottom flask for rotary evaporation. Upon solvent removal and washing of the dried solid material with diethyl ether, a sample of enriched endohedrals (5 mg) was obtained and labeled as the round 1 precipitate.

For a second round (26 h) of precipitation, anhydrous MgCl₂ (5.6 g) was added to the round 1 filtrate to generate a sample of enriched endohedrals (10 mg), of which CeLu₂N@C₈₀ was a dominant species. A third round (48 h) of fractionation was done by adding anhydrous MgCl₂ (7.5 g) to the round 2 filtrate.

Isolation of CeLu₂N@C₈₀ with SAFA (stage 2)

For purification of CeLu₂N@C₈₀, the recovered precipitate (10 mg) obtained after round 2 of MgCl₂ treatment was added to a 250 mL round bottom flask and dissolved into xylenes (135 mL), which was freshly opened and used directly from the manufacturer. While stirring, freshly dried monoaminosilica gel (MASG, 14.4 g), which had just been vacuum-oven dried overnight at 60 °C and cooled to room temperature, was added to this vigorously stirring solution of round 2 precipitate. The importance of using freshly dried aminosilica and anhydrous solvents for SAFA experiments was recently reported.^[72] After 48 h of fullerene uptake time, the reaction mixture was filtered. Solvent removal of the filtrate by rotary evapora-

Figure 5. Top: the molecular components of CeLu₂N@I_h-C₈₀·Ni(OEP)·2C₇H₈ drawn with 50% thermal contours. The toluene molecules, hydrogen positions, and disordered components are omitted for clarity. Bottom: the orientation of the CeLu₂N cluster with respect to the plane of the [Ni(OEP)] molecule.

tion and subsequent washing of the dried powder with diethyl ether produced $\text{CeLu}_2\text{N@C}_{80}$ (4 mg, 95% purity). If further purity is desired, a single injection into a HPLC column (Supporting Information) readily produces a sample of 99% purity.

HPLC monitoring of reaction mixtures

To determine when to stop a SAFA reaction and begin filtration, aliquots from the reaction mixture are taken at arbitrary times and immediately injected for HPLC monitoring for loss of contaminants (i.e., decrease of contaminant peak areas relative to the peak area of $\text{CeLu}_2\text{N@C}_{80}$). Chromatographic conditions were as follows: PYE or BuckyPrep-M stationary phases (4.6 mm x 250 mm, SES research), 360 nm UV detection, and xylenes as a mobile phase (1 mL min⁻¹).

MALDI mass spectrometry

Mass spectral characterization was achieved on a Bruker Microflex LT mass spectrometer. Endohedral samples were dissolved in CS_2 and spotted directly onto a stainless steel target using 1–5 μL of fullerene solution. No matrix was used. Upon drying, the target was inserted into the spectrometer for MALDI analysis. Data were collected in the positive ion mode.

Single-crystal X-ray diffraction

Crystals were grown by slow diffusion. A filtered solution of $\text{Ni}^{\text{II}}(\text{OEP})$ in toluene was carefully layered over a toluene solution containing $\text{CeLu}_2\text{N@C}_{80}$. Black blocks formed within two weeks. A suitable crystal was mounted in the nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON 100 CMOS detector at beamline 11.3.1 of the Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA). Data were collected with the use of silicon(111) monochromated synchrotron radiation ($\lambda = 0.77490 \text{ \AA}$). The data set was reduced with the use of Bruker SAINT, and a multiscan absorption correction was applied with the use of SADABS. The structures were determined by direct methods and refined by full-matrix least squares on F^2 (SHELXL-2014).^[84] Some low-angle reflections were omitted because of overload or beamstop blockage. The structure was refined as a two-component twin (010100001) with a refined twin parameter of 0.4588(6). See the Supporting Information for further refinement details.

Crystal description = black block; crystal size = $0.09 \times 0.09 \times 0.08 \text{ mm}$; crystal system, triclinic; space group, $P\bar{1}$ $Z=2$; $a = 14.6197(7)$, $b = 14.6402(7)$, $c = 20.4342(9) \text{ \AA}$, $\alpha = 83.044(3)$, $\beta = 83.135(2)$, $\gamma = 60.635(2)^\circ$; $V = 3774.5(3) \text{ \AA}^3$; $\rho_{\text{calcd}} = 1.971 \text{ g cm}^{-3}$; $F(000) = 2206$; $\mu = 4.365 \text{ mm}^{-1}$; $\lambda = 0.77490 \text{ \AA}$; Φ and ω scans; $2\theta_{\text{max}} = 80.444^\circ$; $T = 100(2) \text{ K}$; 88455 reflections collected; 35935 independent reflections ($R_{\text{int}} = 0.0278$) included in the refinement; $R_1 = 0.0598$ for $I > 2\sigma(I)$; $wR_2 = 0.1538$ for all data; 1331 parameters and 720 restraints; CCDC 1052613 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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