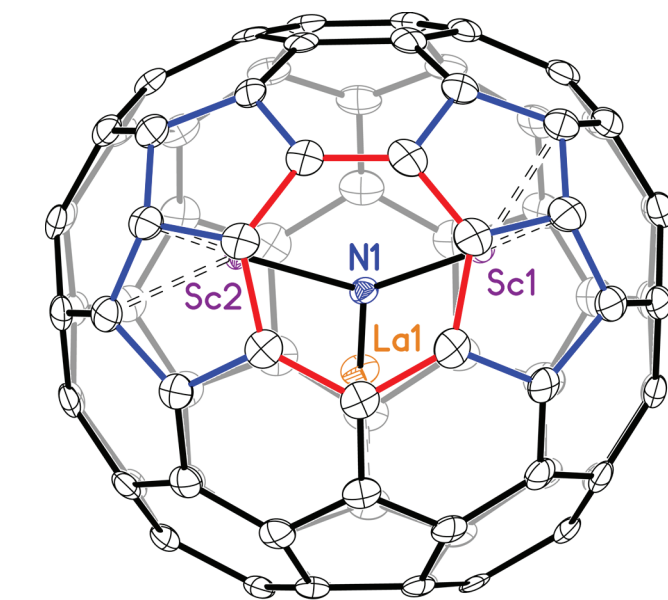


# A Fullerene that Breaks the Rules

In the 30 years since the discovery of the classic fullerene "buckyball" of 60 carbon atoms, scientists have found many variations on the fullerene theme: carbon nanotubes (elongated buckyballs), endohedral fullerenes (buckyballs with molecules inside), and even carbon "peapods" (nanotubes with buckyballs inside). Within this great diversity, however, certain rules emerged. One such rule governed the number and placement of the pentagonal and hexagonal carbon rings that are the basic fullerene building blocks. Now, scientists have used small-molecule x-ray crystallography at the ALS to verify and characterize a new rule-breaking fullerene that incorporates a seven-membered (heptagonal) carbon ring. This new molecule changes the definition of a classical fullerene and expands the range of structural possibilities for endohedral fullerenes, which have desirable physical properties with applications in solar cells, image contrasting, and medicine.

Fullerenes are a unique form of carbon consisting of molecular cages (two other forms, or allotropes, of carbon are diamond and graphite). This class of molecular cages can contain atoms inside (indicated by the symbol "@" in the fullerene name), or they can react with other molecules that



**The x-ray crystal structure of  $\text{LaSc}_2\text{N}@C_s(\text{hept})\text{-C}_{80}$  showing the heptagon (red) and two pentagonal units (blue).**

bind to the surface of the cage. Both changes can affect the physical properties of the complex as a whole. Endohedral fullerenes with an interior cluster of the form  $\text{M}_3\text{N}$  ( $\text{M}$  = metal,  $\text{N}$  = nitrogen) and an 80-carbon cage typically possess highly symmetrical carbon cages, where the specific type of symmetry (the point group) is designated by the notation  $I_h$  or  $D_{5h}$ . The first fullerene discovered in 1985, the iconic 60-carbon molecular soccer ball, is designated as  $I_h\text{-C}_{60}$ . Fullerenes in the  $I_h$  and  $D_{5h}$  point groups are isomers

(molecules with same chemical formula but different structures) that obey the isolated pentagon rule (IPR), in which every pentagonal ring is surrounded by hexagonal rings. Their molecular symmetries and structures can be verified via single-crystal x-ray diffraction.

In this work, researchers identified a rule-breaking mixed-metal fullerene using small-molecule x-ray diffraction at ALS Chemical Crystallography Beamline 11.3.1. This fullerene,  $\text{LaSc}_2\text{N}@C_s(\text{hept})\text{-C}_{80}$ , was prepared via arc discharge between graphite rods doped

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with  $\text{La}_2\text{O}_3$  and  $\text{Sc}_2\text{O}_3$ . The results showed that  $\text{LaSc}_2\text{N}@C_s(\text{hept})\text{-C}_{80}$  breaks the rules that define classical fullerenes in that it contains a heptagon in its ring system, giving it a different point-group symmetry ( $C_s$ ). Generally, fullerenes are composed of only pentagonal



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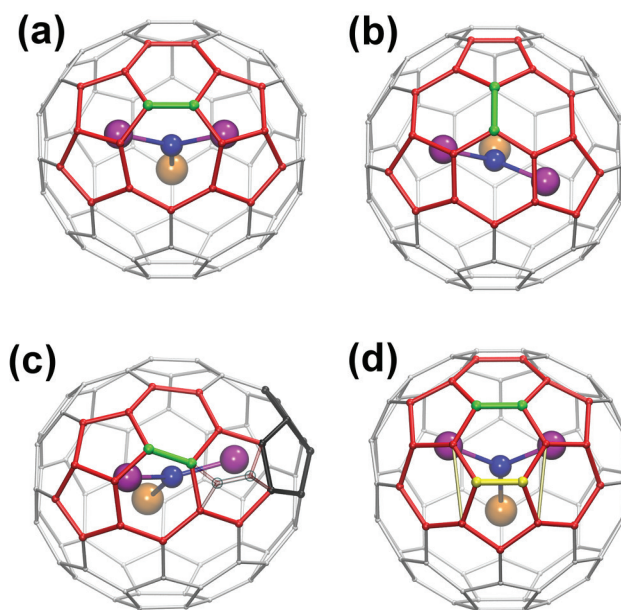
## Playing Catch with Buckyballs

**Q: How do you catch a buckyball?**

**A: With a molecular catcher's mitt!**

Crystallography is a great way to study the structure of large molecules such as endohedral fullerenes. Unfortunately, crystallized fullerene molecules are not stationary, but tend to spin in place within the crystal lattice, smearing out the diffraction data. To decrease this rotational disorder, scientists co-crystallize the fullerenes with something else. A porphyrin is an organic molecule that can form a bowl-shaped catcher's mitt that stabilizes fullerene molecules when co-crystallized.

With the fullerenes securely caught, researchers can begin to sort out how their various structures relate to their many potentially useful properties. Carbon-based, highly stable, and hollow, fullerenes are a natural fit in medicine as a vehicle for delivering radiotracers for imaging or radiopharmaceuticals for treatment of diseases. Fullerenes also have a high electron affinity, and show great promise as electron-acceptor material in organic photovoltaic applications, i.e. cheap, efficient plastic solar cells. Other potential applications include superconductors, nanomemory devices, quantum computers, and more.



**a)** Molecular structure of  $\text{LaSc}_2\text{N}@C_5(\text{hept})\text{-C}_{80}$ , with Sc = magenta, La = orange, and N = blue. **(b)** The related isomer,  $\text{LaSc}_2\text{N}@I_h\text{-C}_{80}$ . The  $C_5(\text{hept})$  cage in (a) can be rearranged into the isomer in (b) by rotation of the C–C bond highlighted in green. **(c)** The  $C_5(\text{hept})$  cage can also be transformed into this  $\text{LaSc}_2\text{N}@C_{78}$  structure by removal of one  $C_2$  fragment (shown in outline). **(d)** Adding a  $C_2$  fragment (yellow) results in this  $\text{LaSc}_2\text{N}@C_{3v}(8)\text{-C}_{82}$  fullerene, which may be a  $C_5(\text{hept})$  cage precursor.

and hexagonal rings, which mathematically agrees with Euler's theorem, according to which every fullerene contains 12 pentagons, with the remaining rings being hexagons. In the new fullerene, there are also two pentalene units that violate the IPR by having abutting pentagons. The presence of a heptagon and two pentalene units forces the structure to have an unprecedented

13 pentagons in total. Nevertheless, this molecule is still classified as a fullerene, since it consists of an all-carbon cage.

Two other isomers,  $\text{LaSc}_2\text{N}@I_h\text{-C}_{80}$  and  $\text{LaSc}_2\text{N}@D_{5h}\text{-C}_{80}$ , were also isolated. Historically, these are the two most common isomers of the  $M_3N@C_{80}$  cage, with the  $I_h$  isomer being far more prevalent than  $D_{5h}$ . The appearance of the  $C_5(\text{hept})$  isomer was not antici-

pated. However, computational analysis for  $\text{LaSc}_2\text{N}@C_{80}$  suggests that, while the  $I_h$  cage is lowest in relative energy, the  $C_5(\text{hept})$  cage is only 27 kJ/mol less stable, and the  $C_5(\text{hept})$  cage is 34 kJ/mol more stable than the  $D_{5h}$  cage. Thus, previous failure to isolate the  $C_5(\text{hept})$  cage may be ascribed to kinetic factors rather than to thermodynamic stability. The researchers proposed that a low

yield of the  $C_5(\text{hept})$  cage would arise if it has a low barrier to rearrangement into other isomers. Several different rearrangements are possible, all of which have a bearing on the still-unknown mechanism for the synthesis of multiple products in the plasma of the arc-discharge process. Now that the new heptagonal isomer has been characterized, the search is on for other examples.

