

La@C₈₂ Anion. An Unusually Stable Metallofullerene

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Endohedral metallofullerenes have attracted special interest since their first proposal in 1985.¹ Smalley and co-workers showed in 1991 that several lanthanum-containing fullerenes can be produced, and that extraction with toluene yields mostly La@C₈₂.² Since then, La@C₈₂ has been extensively investigated as the prototype of isolable metallofullerenes, but its structure is still unknown.³ Although M@C₈₂ (M = group 3 or lanthanide metals) have been isolated and purified in macroscopic quantities, their instability in air has prevented detailed experimental characterization.⁴ Here we report that the anion of La@C₈₂ has a unique stability toward air and water. The structure of La@C₈₂ is determined from NMR measurements of the stable anion and density functional calculations.

Bulk controlled potential electrolysis of La@C₈₂^{4b} was used to prepare the anion. No ESR signal was observed at 124 K for La@C₈₂(-), unlike La@C₈₂,⁵ which indicates that La@C₈₂(-) is diamagnetic. The anion of the second isomer^{4c} was also highly

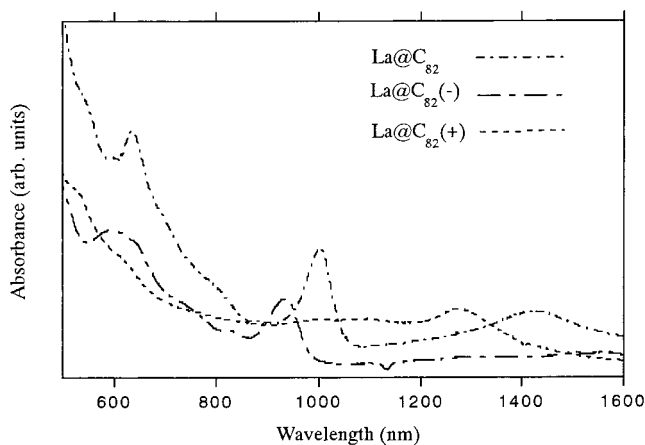


Figure 1. Vis-near-IR absorption spectra of La@C₈₂, La@C₈₂(-), and La@C₈₂(+).

stable and diamagnetic. The cations of two La@C₈₂ isomers were prepared and isolated in the same way. To our knowledge, these are the first examples for the isolation of reduced or oxidized forms of M@C₈₂.⁶ As an extension, we have also prepared the anion and cation of two Pr@C₈₂ isomers that were recently purified.⁷

The absorption spectra of La@C₈₂, La@C₈₂(-), and La@C₈₂(+) are shown in Figure 1. La@C₈₂ shows broad absorption bands over the entire near-IR region down to 2300 nm⁴ because of its open-shell electronic structure, described formally as La³⁺C₈₂³⁻.⁸ A significant color change from dark brown to dark green was observed during reduction of La@C₈₂. La@C₈₂(-) has an onset of a band around 1600 nm, a near-IR band at 930 nm, and a broad visible band at 580 nm. The color and absorption spectrum of La@C₈₂(-) did not change after 4 months in air, while those of La@C₈₂(+) was invariant for only several hours at room temperature under argon.

A degassed solution of La@C₈₂(-) in *o*-dichlorobenzene was heated in a sealed tube at 170 °C for 10 min, or photoirradiated above 400 nm at 20 °C. In both cases, the absorption spectrum remained unchanged. When the solution was irradiated above 300 nm, the absorption spectrum immediately became featureless. Interestingly, a La@C₈₂ peak appeared in the positive ion FAB mass spectrum of this photolyzed solution, suggesting that dimerization and/or oligomerization occurs during photoirradiation.

The absorption spectrum of La@C₈₂(-) was unchanged not only in water but also in an ODCB solution of phenol (pK_a = 10), thiophenol (pK_a = 8), *p*-nitrophenol (pK_a = 7), acetic acid (pK_a = 5), and 2,4-dinitrophenol (pK_a = 4). La@C₈₂(-) was oxidized to give La@C₈₂ in an ODCB solution of dichloroacetic acid (pK_a = 1).⁹ This suggests that La@C₈₂(-) may survive even in acidic solution (pK_a ≥ 4).

Because of the difficulty in preparing single crystals, NMR measurements are most useful for structural determination,³ but have not been utilized for La@C₈₂ due to its paramagnetic nature. However, the high stability and diamagnetic nature of La@C₈₂(-) allow NMR determination of the structure of La@C₈₂. The ¹³⁹La NMR spectrum of La@C₈₂(-) exhibits a single peak in

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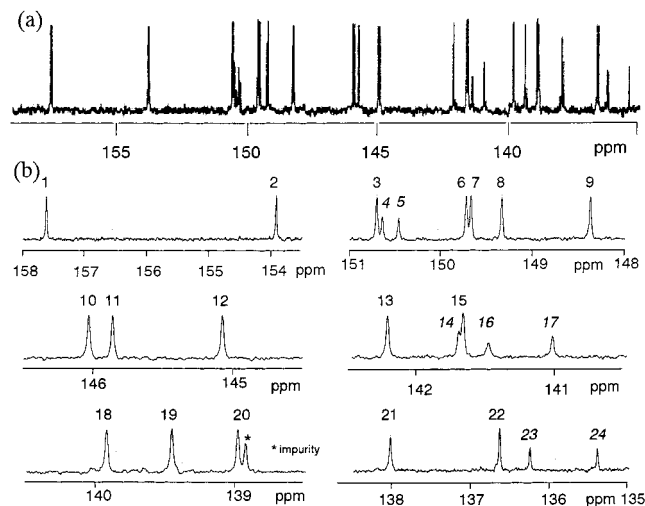


Figure 2. (a) ^{13}C NMR spectrum of $\text{La@C}_{82}(-)$ and (b) its expanded views.

d_4 -ODCB at 300 K with a line width of ~ 2600 Hz. The chemical shift at -470 ppm is close to that at -403 ppm observed for $\text{La}_2@\text{C}_{80}$.¹⁰ This may suggest that La has a similar formal charge in $\text{La@C}_{82}(-)$ and $\text{La}_2@\text{C}_{80}$.^{8,11}

The C_{82} fullerene has nine distinct isomers (C_{3v} (a), C_{3v} (b), C_{2v} , C_2 (a), C_2 (b), C_2 (c), C_s (a), C_s (b), and C_s (c)) that satisfy the isolated pentagon rule¹² (see ref 13 for these structures). Since the ^{13}C NMR study of C_{82} shows only one isomer with C_2 symmetry is abundantly produced,¹⁴ it was once assumed that La was encapsulated inside the abundant isomer. Because of the three-electron transfer from La to C_{82} , however, it was recently predicted that encapsulation of La inside the C_{2v} , C_{3v} (b), or C_s (c) isomers is energetically much more favorable, which leads to C_{2v} , C_{3v} , and C_s symmetry, respectively.⁸ These endohedral structures have 24 [17(4) + 7(2)], 17 [11(6) + 5(3) + 1(1)], and 44 [38(2) + 6(1)] nonequivalent carbons, respectively, where the value in parentheses is the relative intensity. As Figure 2 shows, the 125 MHz ^{13}C NMR spectrum of $\text{La@C}_{82}(-)$ exhibits 17 distinct lines of near-equal intensity and 7 lines of half the intensity, verifying clearly that La@C_{82} has C_{2v} symmetry. This agrees with the fact that the C_{2v} structure is energetically most stable.⁸

The C_{2v} structure of La@C_{82} was optimized at the BLYP level¹⁵ and identified as an energy minimum from frequency calculations. As Figure 3 shows, La@C_{82} is most energetically stabilized when La approaches the center of one hexagonal ring in C_{82} along the C_2 axis. This is consistent with the EXAFS study of La@C_{82}

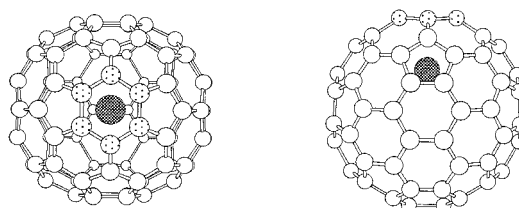


Figure 3. Two views of the optimized structure of $\text{La@C}_{82} (C_{2v})$.

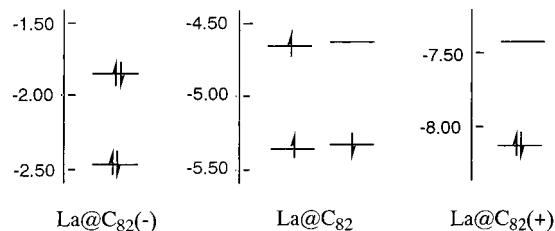


Figure 4. Orbital diagrams in eV.

which shows that the number of nearest neighbor carbons is six.¹⁶ The same was calculated at the BLYP level for $\text{La@C}_{82}(-)$ and $\text{La@C}_{82}(+)$, confirming that La@C_{82} maintains C_{2v} symmetry even upon reduction and oxidation. The distances between La and the hexagonal carbons were calculated to be 2.638 and 2.646 Å for La@C_{82} . These differ little from those of 2.636 and 2.643 Å for $\text{La@C}_{82}(-)$ and 2.640 and 2.649 Å for $\text{La@C}_{82}(+)$, suggesting that the La position is only little changed upon either reduction or oxidation.

As Figure 4 shows, La@C_{82} has an open-shell structure. Reduction and oxidation take place on the carbon cage of La@C_{82} ,¹⁷ leading to a closed-shell electronic structure of $\text{La@C}_{82}(-)$ and $\text{La@C}_{82}(+)$. Therefore, these ions have no radical character, as confirmed by the ESR study. This is consistent with the fact that $\text{La@C}_{82}(-)$ is air-insensitive. The observation that $\text{La@C}_{82}(+)$ is less stable in air than $\text{La@C}_{82}(-)$ is probably due to the lower LUMO level of $\text{La@C}_{82}(+)$.

In conclusion, La@C_{82} becomes diamagnetic and remarkably stable due to the closed shell structure obtained upon reduction. The ^{13}C NMR spectrum of the anion reveals that La@C_{82} has C_{2v} symmetry. ^{13}C NMR measurements of paramagnetic metallofullerenes in anionic forms may be widely applicable for structural determination.¹⁸ Isolation of anionic metallofullerenes is a stepping-stone on the way to developing biological applications and new materials.

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Supporting Information Available: Preparation and spectroscopic data of the anion and cation of La@C_{82} (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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