Networked and Endohedral $La_2C_n^+$ (n = 28−100) Metallofullerenes

Konstantin B. Shelimov and Martin F. Jarrold*

Department of Chemistry, Northwestern University
2145 Sheridan Road, Evanston, Illinois 60208

Received March 27, 1995

One of the central issues in the study of metallofullerenes[1] is the location of the metal atom, i.e., inside the cage, outside the cage, or in the carbon network, and how this varies with the nature of the metal atom, the number of metal atoms, and the size of the fullerene. For gas phase LaC_n^+ metallofullerenes, ion mobility measurements have shown that the La atom is always endohedral, unless the fullerene cage is too small to encapsulate it (less than around 36 carbon atoms).[2] Studies of the geometries of $La_2C_n^+$ (n = 28−100) metallofullerenes, reported here, indicate that the driving force for encapsulation of a second metal atom is much lower than that for the first one. A mixture of fullerenes with one and two endohedral metal atoms is produced even for large LaC_n^+ clusters with an even number of carbon atoms, where the carbon cage can easily accommodate two lanthanum atoms, and no evidence is found for the formation of diendohedral fullerenes with an odd number of carbon atoms. The reduced efficiency for encapsulation of the second lanthanum atom probably results from electrostatic repulsion between the metal atoms.

Extractable $M@C_{82}$ (M = Sc, Y, La)[3] metallofullerenes are by far the best-characterized metallofullerene species.[4−7] Metallofullerenes containing multiple metal atoms are more difficult to produce and separate, although significant progress has recently been made in the purification of some discandium metallofullerenes.[8] Several studies of $Sc_2@C_{82}$, $Sc_2@C_{84}$, $Y_2@C_{82}$ (in a mixture with $Y@C_{82}$), and $Sc_3@C_{82}$ fullerenes have recently been reported.[5,7,9−12] The only extractable dilanthanum metallofullerene reported so far is La_2C_{80}.[13] Its structure remains uknown. Alvarez *et al.*[13] have speculated that the series of extractable La_nC_{84-2n} (n = 0−2) fullerenes may be due to networked species. To understand the structures and stabilities of metallofullerenes, it is really necessary to study a broader range of these species. This can be most easily accomplished by studying them in the gas phase, where ion mobility measurements[14] can be used to probe the location of the metal atoms. This approach has recently been used to examine $LaC_n^{+\,2}$ and $NbC_n^{+\,15}$ metallofullerenes.

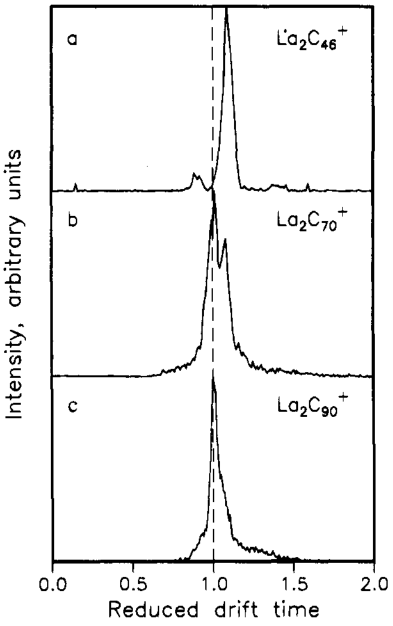

Figure 1. Drift time distributions of $La_2C_{46}^+$, $La_2C_{70}^+$, and $La_2C_{90}^+$ recorded at an injection energy of 300 eV. The reduced drift times were obtained by dividing the drift times of $La_2C_n^+$ clusters by those measured for the C_n^+ fullerenes. The peaks with the reduced drift times around 1.1 and 1.0 are assigned to $La_2C_n^+$ fullerenes with one and two endohedral metal atoms, respectively. The low-intensity features at larger drift times correspond to non-fullerene isomers. Most of the non-fullerene isomers are annealed into fullerenes at this injection energy.[18]

The experimental apparatus has been described in detail elsewhere.[16] La-containing carbon cluster cations are generated by the laser vaporization of a composite LaC_2/graphite rod. In some experiments an electron gun was employed to increase the cluster ion signals. The clusters are mass-selected and injected into a drift tube containing He buffer gas. High (250−300 eV) injection energies were used so that the clusters were significantly annealed by the transient collisional heating that occurs as they enter the drift tube. The clusters then drift slowly across the drift tube under the influence of a weak electric field. Isomers with different shapes (such as endohedral and nonendohedral metallofullerenes) have different mobilities and are separated in the drift tube. The drift tube was cooled to around 80 K to increase the resolution. Upon exiting the drift tube the cluster cations are mass-analyzed and detected with an off-axis collision dynode and dual microchannel plates.

Figure 1 shows the drift time distributions for several $La_2C_n^+$ clusters recorded with an injection energy of 300 eV. From comparison with the previously analyzed drift time distributions for C_n^+ and LaC_n^+ clusters,[2,17] we assign the major peaks present in the distributions in Figure 1 to fullerene isomers. At an injection energy of 300 eV, most of the non-fullerene isomers have annealed into fullerenes.[18] The dashed line in Figure 1 shows the drift time of the corresponding pure carbon fullerenes. For $La_2C_{46}^+$, the dominant peak in the distribution occurs at

---

[1] For a recent review, see: Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

[2] Shelimov, K. B.; Clemmer, D. E.; Jarrold, M. F. *J. Phys. Chem.* **1994**, *98*, 12819.

[3] Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

[4] Johnson, R. D.; de Vries, M. S.; Salem, J. R.; Bethune, D. S.; Yannoni, C. S. *Nature* **1992**, *355*, 239.

[5] Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460.

[6] Soderhom, L.; Wurz, P.; Lykke, K. R.; Parker, D. H.; Lytle, F. W. *J. Phys. Chem.* **1992**, *96*, 7153.

[7] Park, C.-H.; Wells, B. O.; DiCarlo, J.; Shen, Z.-X.; Salem, J. R.; Bethune, D. S.; Yannoni, C. S.; Johnson, R. D. de Vries, M. S.; Booth, C.; Bridges, F.; Pianetta, P. *Chem. Phys. Lett.* **1993**, *213*, 196.

[8] Shinohara, H.; Yamaguchi, H.; Hayashi, N.; Sato, H.; Ohkohchi, M.; Ando, Y.; Saito, Y. *J. Phys. Chem.* **1993**, *97*, 4259.

[9] Yannoni, C. S.; Hoinkis, M.; de Vries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, *256*, 1191. Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y.; *Nature* **1992**, *357*, 52.

[10] Shinohara, H.; Sato, H.; Saito, Y.; Ohkohchi, M.; Ando, Y. *J. Phys. Chem.* **1992**, *96*, 3571.

[11] Shinohara, H.; Hayashi, N.; Sato, H.; Saito, Y.; Wang, X.-D.; Hashizume, T.; Sakurai, T. *J. Phys. Chem.* **1993**, *97*, 13438.

[12] Beyers, R.; Kiang, C.-H.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Harich, K.; Stevenson, S. *Nature* **1994**, *370*, 196.

[13] Alvarez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 10561.

[14] Hagen, D. F. *Anal. Chem.* **1979**, *51*, 870. Karpas, Z.; Cohen, M. J.; Stimac, R. M.; Wernlund, R. F. *Int. J. Mass Spectrom. Ion Processes* **1986**, *83*, 163. von Helden, G.; Hsu, M. T.; Kemper, P. R.; Bowers, M. T. *J. Chem. Phys.* **1991**, *95*, 3835. For a recent review, see: St. Louis, R. H.; Hill, H. H. *Crit. Rev. Anal. Chem.* **1990**, *21*, 321.

[15] Clemmer, D. E.; Hunter, J. M.; Shelimov, K. B.; Jarrold, M. F. *Nature* **1994**, *372*, 248.

[16] Jarrold, M. F.; Bower, J. E.; Creegan, K. *J. Chem. Phys.* **1989**, *90*, 3615. Jarrold, M. F.; Bower, J. E. *J. Chem. Phys.* **1992**, *96*, 9180.

[17] von Helden, G.; Hsu, M. T.; Gotts, N. G.; Bowers, M. T. *J. Phys. Chem.* **1993**, *97*, 8182.

[18] Shelimov, K. B.; Jarrold, M. F. To be published.

0002-7863/95/1517-6404$09.00/0

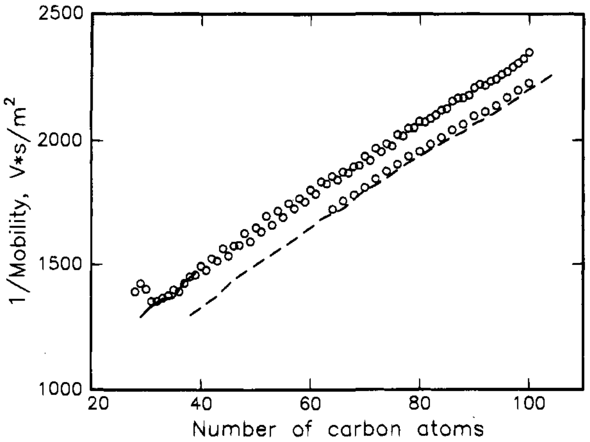

Figure 2. Plot of the inverse mobilities of $La_2C_n^+$ (n = 28−100) fullerenes in helium buffer gas against cluster size. The mobilities were measured with the drift tube at 80 K. The solid line shows the inverse mobilities of nonendohedral LaC_n^+ (n = 29−37) fullerenes, and the dashed line shows the inverse mobilities of pure C_n^+ fullerenes.

slightly longer times than the pure carbon fullerene (the smaller peak at shorter times is probably due to doubly charged species). For $La_2C_{70}^+$, there are two large peaks present in the distribution, one with approximately the same drift time as the corresponding pure carbon fullerene, and one with a longer drift time. For $La_2C_{90}^+$, the peak close to the drift time of the pure carbon fullerene dominates, though the peak at longer times persists as a shoulder.

Figure 2 shows the inverse mobilities of $La_2C_n^+$ (n = 28−100) fullerenes, in helium buffer gas, plotted against cluster size. Only one fullerene isomer is observed in the n = 28−63 size range (see Figure 1a), while two isomers with mobilities that differ by 5−7% are present for larger $La_2C_n^+$ clusters with an even number of carbon atoms (see Figure 1b). Ion mobility studies of LaC_n^+ [2] and NbC_n^+ [15] fullerenes have shown that when the metal atom moves from a nonendohedral position to an endohedral position, the mobility increases by 5−10%. The mobilities of $La_2C_n^+$ (n = 31−37) fullerenes are essentially identical to those of nonendohedral LaC_n^+ fullerenes[2] (plotted as the solid line in Figure 2). This indicates that $La_2C_n^+$ (n = 31−37) metallofullerenes have one metal atom inside the carbon cage, while the other one is either outside the cage or in the carbon network (the $La(La@C_n)^+$ or $La@C_nLa^+$ structure in the symbolism proposed by Chai *et al.*[3]). The $La_2C_{38}^+$−$La_2C_{63}^+$ fullerenes, and the $La_2C_n^+$ ($n \geq 64$) fullerenes with the smaller mobilities, have mobilities which clearly correlate with those of the $La_2C_n^+$ (n = 31−37) fullerenes, so these fullerenes must also have the $La(La@C_n)^+$ or $La@C_nLa^+$ structure.

More information about the structures of the fullerenes with one endohedral metal atom can be obtained from studies of the unannealed isomer distributions and the dissociation patterns.[18] For clusters with 36−63 carbon atoms, fullerenes with an odd number of carbon atoms are substantially more abundant in the unannealed isomer distributions than those with an even number of carbon atoms. This suggests that the former are stabilized by the nonendohedral La atom occupying the defect site in the carbon network (the $La@C_nLa^+$ structure). A similar networked geometry has been proposed for small LaC_n^+ and all NbC_n^+ fullerenes with an odd number of carbon atoms.[2,15] $La_2C_{32}^+$ and $La_2C_{34}^+$ clusters lose C_{4m+2} (m = 2−5) fragments rather than La^+ when they dissociate, while La^+ is the dominant dissociation product for larger $La_2C_n^+$ ($36 \leq n \leq 62$) clusters with an even number of carbon atoms. Since $La@C_{36}^+$ is the smallest *stable* endohedral LaC_n^+ metallofullerene, this dissociation pattern suggests that the nonendohedral La atom is also a part of the carbon network in $La_2C_{32}^+$ and $La_2C_{34}^+$ fullerenes, creating more room for the endohedral metal atom. Finally, Figure 2 shows that, for $La_2C_n^+$ (n = 40−80) fullerenes with one metal atom inside the cage, the mobilities of the species with an even number of carbon atoms are systematically about 1% smaller than those of the species with an odd number of carbon atoms, while no such variation is observed for smaller clusters. This suggests that for $La_2C_n^+$ (n = 40−80) fullerenes with an even number of carbon atoms the second metal atom is in an exohedral position (the $La(La@C_n)^+$ structure), where its effect on the fullerene mobility is expected to be the largest. The odd−even variation in the mobilities of $La_2C_n^+$ fullerenes with one endohedral metal atom seems to disappear for $n > 80$ (see Figure 2). However, for $La_2C_n^+$ ($n > 80$) clusters with an even number of carbon atoms these species are not resolved as separate peaks in the drift time distributions (see Figure 1c), so that their mobilities can be determined only approximately.

The mobilities of $La_2C_{28}^+$ and $La_2C_{29}^+$ fullerenes are smaller than the mobilities of the corresponding nonendohedral LaC_n^+ fullerenes by about 10% (see Figure 2). We therefore assign $La_2C_{28}^+$ and $La_2C_{29}^+$ fullerenes to geometries where both metal atoms are nonendohedral. Unlike pure C_n^+ fullerenes, dilanthanum metallofullerenes with 28 and 29 carbon atoms are easily observable in our experiments, which implies that the metal atoms occupy positions in the carbon network, reducing the strain energy of these small fullerenes. The mobility of $La_2C_{30}^+$ fullerene lies between the mobilities expected for the structures with one and two nonendohedral metal atoms, so that we cannot unambiguously determine the position of the metal atoms in this fullerene.

The mobilities of the "faster" fullerene isomer of clusters with an even number of carbon atoms, which is first observed for $La_2C_{64}^+$, are within 1.5% of those of the pure carbon fullerenes (plotted as the dashed line in Figure 2). Therefore we assign this isomer to the endohedral $La_2@C_n^+$ structure. The size of the smallest endohedral fullerene we observe ($La_2@C_{64}^+$) is close to that determined by laser "shrink-wrapping" experiments ($La_2@C_{66}^+$).[3] The abundance of the fullerenes with two endohedral La atoms, relative to those with one endohedral metal atom, increases substantially when the electron gun is employed, suggesting that the former have higher ionization potentials. The relative abundance of the $La_2@C_n^+$ geometry increases sharply with cluster size for even-numbered clusters with $n > 64$, to reach around 70% for $La_2C_{78}^+$. However, a rather intense shoulder, attributable to a fullerene with one endohedral metal atom, is present on the $La_2@C_n^+$ peaks in the drift time distributions of all large $La_2C_n^+$ clusters with an even number of carbon atoms (see Figure 1c). Thus the relative abundance of the $La_2@C_n^+$ structure does not exceed 70−75% even for the largest clusters studied. The drift time distribution for $La_2C_{80}^+$ (the only known extractable dilanthanum metallofullerene) is not significantly different from that of its neighbors.

The results presented above indicate that the efficiency of encapsulation of a second La atom inside a fullerene cage is substantially lower than that of the first. While only endohedral fullerenes are observed for LaC_n^+ ($n > 37$) clusters,[2] we observe both diendohedral fullerenes and fullerenes with one nonendohedral metal atom even for large $La_2C_n^+$ clusters with an even number of carbon atoms, and we find no evidence for the formation of $La_2@C_n^+$ species for clusters with an odd number of carbon atoms. The electrostatic repulsion between the endohedral metal atoms, both of which are expected to donate significant electron density to the carbon cage,[19] is one of the likely reasons for the observed behavior. The reduced efficiency for encapsulating the second lanthanum atom could also result from stabilization of the $La(La@C_n)^+$ or $La@C_nLa^+$ geometries by the endohedral lanthanum atom. For example, the extra valence electron available to the networked La atom in the $La_2C_n^+$ system, compared to the LaC_n^+ system, may stabilize the networked structure relative to the endohedral one.

Acknowledgment. We gratefully acknowledge the support of this work by the National Science Foundation (Grant No. CHE-9306900) and the Petroleum Research Fund (administered by the American Chemical Society).

JA950982L

---

[19] Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1994**, *231*, 319.