High-Pressure Toluene Extraction of La@C_n for Even n from 74 to 90

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Received January 12, 1994
Revised Manuscript Received April 12, 1994

In this communication we report the toluene extraction of La@$C_{n=74\text{–}90\ (\text{even } n \text{ only})}$ with a high-temperature, high-pressure extraction technique previously[1,2] used to extract empty giant fullerenes. We have become interested in the unusual properties that endohedral metallofullerenes may exhibit due to the relatively unhindered motions of metal ions[3] trapped within fullerene cages.

Lanthanum-containing fullerenes were first observed within a week[4] of the initial discovery of the special stability of C_{60} and the proposal of its soccerball structure.[5] After the development of the Kratschmer–Huffman method[6] for producing macroscopic quantities of fullerenes, it was shown[7] that arc vaporization could be used to prepare La@C_n. Despite much effort, the isolation of endohedral La@C_n has proved to be difficult, and only very recently have Kikuchi et al.[8] reported the chromatographic separation of La@C_{82}.

Early work[7] indicated that the La@C_{82} species was unique in that it was the only soluble endohedral lanthanum buckyball. It has been found that La@C_{82} is soluble in a wide range of solvents, including cold[9] and boiling[7] toluene, carbon disulfide,[9,10] and pyridine.[11] In addition, the use of greater La:C ratios in producing soot has resulted in the toluene-extractable species, La_2C_{80}.[12] Shinohara and co-workers added La@C_{76} to the list of solvent-extractable species by anaerobic sampling methods.[13]

Our own efforts to extract La@C_n directly from soot laden with La@C_n were unsuccessful, apparently not because the species are insoluble. Sublimation[16] of our raw soots (10^{-6} Torr, 600 °C) and subsequent benzene extraction of material sublimed from the raw soot showed behavior similar to that described in the literature, namely enhanced extraction of La@C_{82}. The question of extraction is not so much one of solubility as it is of coaxing the La@C_n away from fullerene-laden soot.

Soot was produced using the arc vaporization method.[6,7,9–11,14] Graphite powder was mixed with La_2O_3 (C:La atomic ratio of 100:1) that had been oven-dried at a temperature of 100 °C. This mixture was vacuum-baked at approximately 60 mTorr for at least 1 h and then pressed into pellets with an apparatus generally employed to make KBr windows. Cylindrical pellets (13 mm in diameter and 8 mm long) were produced in a 13-mm die set (Specac) which was pumped on with a mechanical pump as it was pressed to 20 000 lbs by a hydraulic press (Fred S. Carver Inc.). The pellets were hand-drilled (15/64 twist drill) a few millimeters deep so that they could be pushed onto 6.4-mm-diameter graphite rods. Soot was generated by an arc discharge (105 A AC in a 180 Torr flowing helium atmosphere) between the graphite/La_2O_3 pellet and a 6.4-mm-diameter graphite rod. By this method, 0.2–0.3 g of soot was produced in 1 h with only parital consumption of the pellet. About 50 mL of room-temperature benzene was added to the raw soot with stirring for about five min. The mixture was placed on filter paper (Whatman No. 1) and washed until the filtrate came through nominally clear (~250 mL of benzene was used in total). Approximately 4% of this soot was soluble in benzene, the soluble portion being mostly C_{60} and C_{70}. With soot produced from plain graphite rods, we generally obtain yields of 10–15% with this procedure. Optimal La@C_n yields are obtained by balancing the need to have lanthanum around with the fact that La_2O_3 kills the fullerene making process, hence, the 100:1 carbon-to-lanthanum atom ratio used in the pellets.

La@C_n is coaxed from the prewashed soot with a high-pressure, high-temperature extraction technique which could be called a "bomb" extraction. *Please note that several redundant precautions were used to ensure that this process was accomplished safely.* The length of the stainless steel tubing and the quantity of soot used were chosen initially such that if every carbon atom in the soot were changed into CO_2, the pressure would not be enough to break the stainless steel tube. In addition, the procedure was carried out in a vacuum oven, eliminating the presence of oxygen about the "bomb" and consequently reducing the ramifications of an improperly constructed vessel. About 1 mL of toluene was added to 0.25 g of prewashed soot, resulting in a sludge. The mixture was stuffed into a 3.8-cm length of seamless stainless steel tubing (6.4 mm o.d., 0.89 mm thick, 0.64 mL internal volume). Some of the toluene evaporated in the process. We estimate that the ratio of toluene to soot within the tube was about 2 mL of toluene per gram of soot. A few drops of toluene were added after the tube was filled with the mixture to eliminate as much air as possible before the tube was sealed with Swagelok fittings. The vessel was baked in a vacuum oven (50 mTorr) at 250 °C for 5 h. Using the Antoine relation,[18] we estimate that a pressure of 16.5 atm was produced in the vessel, which is comfortably below the 340-atm pressure limit specification of the tubing. Given a number of successful runs, it would appear reasonable to process larger batches of soot. Afterward, the pressure-treated soot was removed from its vessel and mixed at 1 atm with ~30 mL of room-temperature toluene for 5 min. The mixture was placed on filter paper (Whatman No. 1) and washed with toluene, producing about 100 mL of a yellow-brown solution. After evaporation of the toluene, one finds a brownish-black

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0002-7863/94/1516-4987$04.50/0

material (bomb extract), which represents 0.3% of the original soot. This toluene bomb extract is laden with a wide range of La@C_n and readily dissolves back into toluene.

Analysis of the toluene extract of the lanthanum bomb soot was accomplished by laser desorption Fourier transform ion cyclotron resonance mass spectrometry (LD/FT/ICR/MS). The mass spectrum was taken with an Extrel FTMS-2000 instrument equipped with dual 4.76-cm cubic traps and a magnetic field strength of 3.0 T. The bomb extract was redissolved in toluene and applied to the mass spectral probe. As the toluene evaporated, a thin[17] layer of material was left to be ionized in the mass spectrometer using a 1.064-μm YG-600A Nd:YAG laser with 120 mJ/pulse.[15] The positive ion mass spectrum shown in Figure 1 is dominated by La@C_{82}^+ but also shows other La@C_n^+, including n = 74, 76, 78, 80, 84, 86, 88 and 90. No mass spectral procedures were employed which discriminated against C_{60} and/or C_{70}. Analysis of mass spectral peak intensities suggests that by mass the material is 20% La@C_n and 11% La@C_{82}. The average size lanthanum-containing fullerene has 82.5 carbon atoms, so the distribution is centered about La@C_{82}. The average size of an empty fullerene in the sample was 100.9 carbon atoms, which is consistent with the facts that the soot was prewashed and that this procedure is good for extracting giant fullerenes.

To confirm the above results, we have burned several samples in oxygen to see how much La_2O_3 is left over. Unfortunately, the thermal gravimetric analysis (TGA) could not be performed on the same sample for which the LD/FT/ICR mass spectrum was recorded. These initial studies suggest that 4–10% of the sample is La@C_n. The bomb extract is not powdery (like low-pressure C_{60}/C_{70} toluene extract), so the amount of toluene trapped in the extract is uncertain. These percentages will rise (and perhaps agree with the mass spectral determination) if there is a significant amount of toluene in the sample. In related experiments[16] on powdery, 1 atm benzene extracts of materials sublimed from soots, we find that LD/FT/ICR/MS characterization suggests 3.0% La@C_{82} content by mass, while TGA suggests 2.4%. So LD/FT/ICR/MS may be overestimating the lanthanum buckyball content, but this is a factor of 2 issue, not an order of magnitude effect. More detailed results are forthcoming.[16]

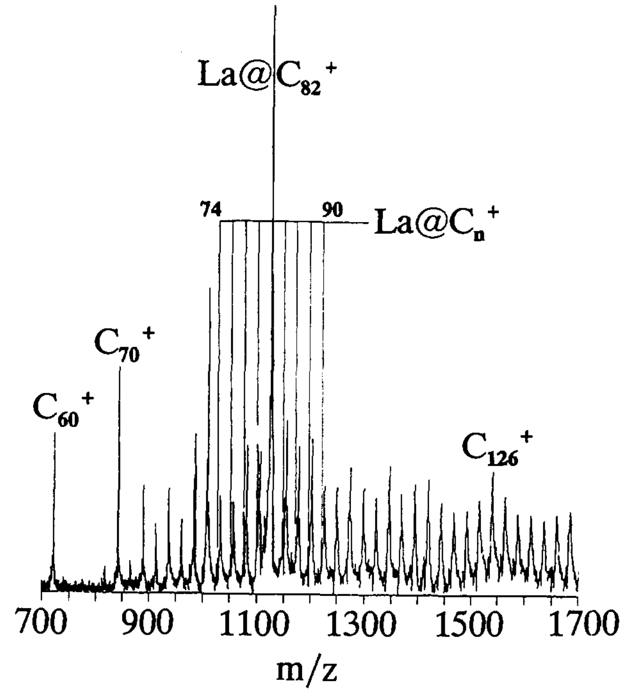

Figure 1. LD/FT/ICR mass spectrum of the positive ions produced upon laser desorption of the toluene "bomb" extract of soot produced by vaporization of graphite and La_2O_3 which was prewashed with benzene. The dominant La@C_{82}^+ peak is accompanied by a range of other size lanthanum-containing fullerenes, all of which are soluble in toluene and have been handled in air.

Clearly, the presently reported "bomb" extract has the highest fraction of endohedral metallofullerene that we have seen by solvent extraction. The La@C_n species can now be studied in solution and are amenable to standard chromatographic techniques.

Acknowledgment. This work was supported by The Ohio State University Center for Materials Research. We would like to thank Patrick K. Gallagher for the thermal analysis of our materials.