Fullerenes with Metals Inside

Yan Chai,[†] Ting Guo, Changming Jin,[†] Robert E. Haufler,[†] L. P. Felipe Chibante,[†] Jan Fure, Lihong Wang,[†] J. Michael Alford, and Richard E. Smalley*

Rice Quantum Institute and Departments of Physics and Chemistry, Rice University, Houston, Texas 77251

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Fullerenes with a single lanthanum atom trapped on the inside of the carbon cage were produced by laser vaporization of a lanthanum oxide/graphite composite rod in a flow of argon gas at 1200 °C. When sublimed with C_{60} and C_{70}, they formed an air-stable film containing principally LaC_{60}, LaC_{70}, LaC_{74}, and LaC_{82}. When dissolved in toluene and exposed to air, LaC_{82} was found to be uniquely stable. Evidence was also obtained for coalescence reactions between these fullerenes at high temperatures to form larger cages with as many as three lanthanum atoms inside. Indications have also been obtained for the successful production of KC_{60}, $C_{59}B$, and $KC_{59}B$ where the boron has substituted for a carbon in the soccerball cage. The use of the @ symbol is advocated for specifying such complex fullerenes as ($K@C_{59}B$).

Introduction

Within a week after the initial 1985 discovery of the special stability of C_{60} and the proposal of its soccerball structure,[1] evidence was obtained in our laboratory that a single lanthanum atom could be trapped inside.[2] Laser vaporization of a graphite target impregnated with $LaCl_3$ produced a supersonic cluster beam that upon intense irradiation with an ArF excimer laser appeared to have one La atom (and only one) attached to each fullerene in a manner such that it could not be knocked off by the laser blast. At the time, the proposal that this tightly bound atom was on the inside triggered some controversy, since a group at Exxon was able to show that two or more atoms could be attached.[3,4] But, in fact, there never was much difference in the results from the two groups. The extra metal atoms in the Exxon experiments were readily blown off by using higher laser power.[4]

Additional very strong confirmation for the geodesic cage structure of fullerenes and the existence of a central metal atom was obtained in a series of "shrink wrap" experiments showing that the carbon cage bursts a point dictated by the ionic radius of the internal atom.[5] Recent experiments by Freiser and coworkers[6,7] have verified that externally attached metal atoms do, in fact, behave in a radically different way: they react readily and are easily knocked off.

Since the discovery by Kratschmer and Huffman last year of a simple method[8,9] for producing macroscopic quantities of C_{60}, C_{70}, and some of the higher empty fullerenes, we have searched for a means of extending this technique to "fill the void" and make macroscopic quantities of internally substituted fullerenes—endohedral fullerene complexes.[10] We report below our first success in this search. It involves a simple revision to the laser-vaporization method originally used in 1985: just do it in an oven at 1200 °C.

Symbolism and Nomenclature

By now the term "fullerene" appears to have achieved uniform acceptance as the general name for hollow carbon structures composed of 12 pentagonal rings and some number of six-membered rings linked together to form a geodesic dome. To discuss the various possible sorts of doped fullerene molecules and materials in a concise fashion, a systematic symbolism and naming convention will need to be worked out. In what follows we need at least to make an initial stab at the first part of this problem.

Ordinarily, a fullerene composed of n carbon atoms with a metal atom, M, will simply be represented as MC_n, regardless of whether the metal atom is inside or outside the cage. However, to facilitate discussion of these and more complicated fullerenes with one or more atoms inside, some attached outside and possibly one or more heteroatoms substituting for carbons in the cage network itself, a more explicit symbolism is essential. We will use a set of parentheses around the symbol @ to indicate that the atoms listed within the parentheses are grouped to form a fullerene. Within this group all atoms listed to the right of the @ symbol are assumed to be part of the cage network, and all to the left are situated somehow inside the cage. Buckminsterfullerene, under this notation is then ($@C_{60}$), and a C_{60}-caged metal species is written ($M@C_{60}$). A more complex example that will be encountered below is $K_2(K@C_{59}B)$, which denotes a 60-atom fullerene cage with one boron atom substituted for a carbon in the geodesic network, a single potassium trapped inside, and two potassium atoms adhering to the outside.

We have adopted this symbolism since it has the virtue of being concise, while still containing the critical information. It is readily printed and transmitted electronically, and it is compatible with ordinary chemical formula conventions. It also has the virtue of being visually suggestive, and it emphasizes the "superatom" aspects of the fullerenes as new chemical entities.

Experimental Section

The laser-vaporization fullerene generator used in this work has been described briefly in an earlier publication.[9] It is simply a 2.5-cm-diameter 50-cm-long quartz tube mounted in a temperature-controlled tube furnace (Lindberg Model 55035). This tube is O-ring sealed on the front end to an aluminum block to which is attached a fused silica window and some plumbing for gas addition and pressure monitoring. Another aluminum block attached at the rear of the quartz tube connects via an adjustable valve to a mechanical vacuum pump. A rotary vacuum feedthrough (Huntington Model VF-106) mounted in the end of this rear aluminum block is attached inside the quartz tube to a 6-mm-o.d. graphite rod that extends through a graphite centering ring into the heated portion of the tube furnace. The end of this graphite rod is threaded into the rear of 1.25-cm-diameter graphite sample rods of the desired composition to serve as targets for vaporization by the laser. During vaporization, the target rod is rotated at 2 rpm in order to maintain a uniform, reproducible

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* To whom correspondence should be addressed.

[†] Robert A. Welch Foundation Predoctoral Fellow.

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surface to the incoming laser beam.

For the experiments described below the vaporization laser was the green second harmonic of a Nd:YAG laser (Quantel) operating at 300 mJ/pulse at 10 pps. The roughly 10-mm diameter nearly Gaussian output beam of this laser was concentrated on the end of the target rod in the furnace using a 50-cm focal length cylindrical lens positioned 60 cm away from the end of the rod, producing an oval vaporization region 1.0 cm high and 0.2 cm wide. As we reported earlier, vaporization of a pure graphite rod in this apparatus produces C_{60}, C_{70}, and a bit of higher fullerenes in excellent yield if the oven is heated to 1200 °C and argon or helium carrier gas at a pressure of several hundred Torr is slowly (0.1–0.2 cm s^{-1}) flowed over the target rod. These fullerenes sublime readily at such temperatures and are carried away in the flowing gas, depositing on cool inner surfaces of the quartz tube at the end of furnace. Argon was used at a pressure of 250 Torr for the vaporization experiments used in this work. With pure graphite targets this resulted in toluene-soluble fullerene yields of well over 10% of the vaporized carbon.

To produce trapped metal fullerenes, composite graphite target rods were made by mixing lanthana powder, La_2O_3 (Aesar AAS grade 99.99%), with graphite powder (Ultra Carbon graphite powder, ultra F purity), together with graphite cement (Dylon Industries, GC grade), and pressing into a 1.25-cm cylindrical die while curing the cement at 100 °C. The resulting rod was then carbonized by slowly heating in argon (1 °C/min to 400 °C, 5 °C/min to 1200 °C) and then baked at 1200 °C for 10 h. In some of the experiments LaB_6 was used in place of the La_2O_3. In others, KCl and/or boron powder was added.

Analysis of the fullerene products was made by Fourier transform ion cyclotron resonance (FT-ICR) study of laser-desorbed sample disks onto which the fullerenes had either been directly sublimed while still in the quartz tube or deposited by evaporating solutions in which the material had been dissolved. The cluster FT-ICR apparatus has been extensively described elsewhere.[11,12] When looking for fullerenes on the target, the vaporization laser (Nd:YAG second harmonic) was kept at low fluence (below 1.0 mJ in a 1-mm-diameter spot on the sample disk). The desorbed clusters were entrained in helium and made into a supersonic beam directed down the central magnetic axis of the FT-ICR device. Ionization was generally accomplished by an ArF excimer laser crossing the neutral cluster beam just before it entered into the analysis magnet. In addition to simply examining their masses, the clusters were probed while levitated in the FT-ICR magnetic trap by pulsing in reactant gases, colliding with argon buffer gas by selective excitation of the cyclotron motion, and irradiating with a XeCl excimer photolysis laser.

Computerization and control of this elaborate cluster FT-ICR facility was recently revamped using a single IBM RISC-6000 Powerstation 320 programmed in C using Xwindows running under the AIX operating system. Copies of the software package and details of the implementation are available from us.

Results and Discussion

Laser vaporization of a 7% (by weight) La_2O_3 in graphite target rod in the tube furnace produced a black-brown deposit on the cool downstream end of the quartz tube. After the furnace was cooled, a water-cooled copper rod with several copper FT-ICR sample disks was then inserted so that the disks were centered in the quartz tube immediately beneath the black-brown deposit. This was done while maintaining a purge of argon gas so that exposure of the freshly generated fullerenes to air was minimized. After pumping down to vacuum (<20 mTorr), the furnace was moved down the quartz tube so that the black-brown deposit was now well within the heated zone, and the temperature was ramped up to 650 °C over 15 min, subliming the fullerenes onto the sample disks and copper support rod. After cooling, the copper rod was removed, and the copper sample disks were found to be covered with a mirrorlike black film. The sublimed film sample was then mounted in the cluster FT-ICR apparatus and pumped down to $<10^{-7}$ Torr.

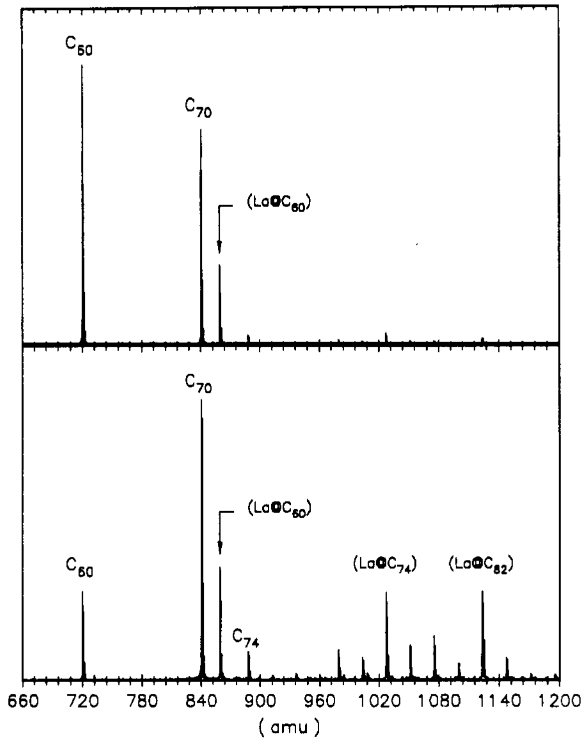

Figure 1. FT-ICR mass spectra of black mirrorlike sublimed fullerene film showing presence of ($La@C_n$) fullerenes. For the top panel the pulsed decelerator responsible for slowing the clusters down to be trapped in the analysis cell was optimized for the C_{60}–C_{70} mass region. For the bottom panel it was optimized for the region around C_{84}.

Figure 1 shows the result of laser-desorption probing of this sublimed film. The top panel FT-ICR mass spectrum was taken with the apparatus optimized to trap clusters in the mass range around C_{70}. Note that both C_{60} and C_{70} are the dominant clusters detected. Under the gentle 0.6-mJ desorption laser conditions used, no signal was detected without the ArF excimer ionization laser. The photon energy of this laser (6.4 eV) is lower than the ionization potentials of C_{60}, C_{70}, and all the other empty fullerenes in this mass range, but they are all very efficiently photoionized by a 1+1 resonant two-photon ionization process with this laser involving the formation of a relatively long-lived triplet state.[13] The absence of signal corresponding to fullerenes less than 60 atoms in size and in the C_{62}–C_{68} range is a good indication that these laser desorption and ArF excimer laser ionization conditions are probing the native composition of the film on the sample disk without fragmentation or fullerene–fullerene reactions.

Note that as labeled in Figure 1 there is a prominent peak corresponding to LaC_{60} present in the film. Careful examination of this feature at high mass resolution showed it had precisely the correct mass and isotope distribution. Exposure to oxygen or ammonia reactant gas in the ICR trap showed no reactivity. Exposure to XeCl excimer light showed it was just as resistant to photofragmentation as C_{60}^+, and when it did fragment, it shrank by successive C_2 losses, just as does C_{60}^+. When this shrinkage was pushed to its limit, it was found to be difficult to fragment past LaC_{44}^+ and impossible to go past LaC_{36}^+ without bursting the cluster. This is a reasonable result for an internally caged lanthanum atom, since the La^+ ionic radius is roughly the same as that of K^+, and $(K@C_{44})^+$ is known to be the smallest survivable $(K@C_n)^+$ cluster.[5] In the case of a tightly shrink-wrapped $(La@C_n)^+$ cluster, the ground electronic state may involve higher

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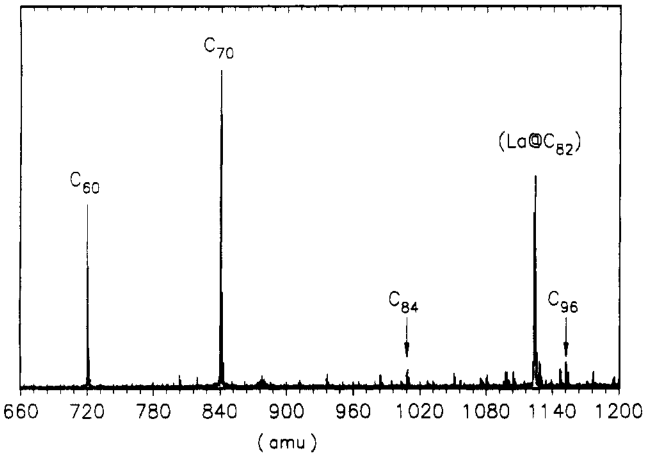

Figure 2. FT-ICR mass spectrum of hot toluene extract of fullerene material produced by laser vaporization of a 10% La_2O_3/graphite composite rod. The sample was exposed to air and moisture.

effective charge on the central metal atom, permitting the "shrink wrapping" to proceed a bit further before the fullerene cage bursts.

We therefore believe that the desired $(La@C_{60})$ clusters had been made in abundance in the quartz tube furnace. They survived the 1200 °C conditions in the furnace during the several minutes necessary to flow to the end where they deposited in the black-brown film. They survived the subsequent sublimation onto the copper sample disk, and when imbedded in a high-quality film made up primarily of C_{60} and C_{70} they survived for several hours exposed to air prior to mounting in the FT-ICR apparatus.

Also evident in the top part of Figure 1 are some small peaks due to higher fullerenes. In the bottom panel, these are seen more clearly after the apparatus had been adjusted to trap them more effectively. Note that, except for C_{74} and a small amount of C_{84}, all this signal is due to $(La@C_n)$ fullerenes, with $(La@C_{74})$ and $(La@C_{82})$ appearing specially abundant. Experiments with reactivity and fragmentation behavior proved all these to have the La atom trapped inside. No larger clusters were found under these conditions of laser desorption. The relative absence of $(La@C_n)$ clusters with $60 < n < 70$ and $n > 84$ is strong evidence that the lasers did not perturb the native $(La@C_n)$ cluster distribution on the sublimed sample film. They too must have been made in the quartz tube furnace and survived sublimation and transport through room air to the FT-ICR apparatus.

The results of Figure 1 give the appearance that a substantial fraction of the sublimed film is made up of $(La@C_n)$-doped fullerenes. However, these species are likely to be directly photoionized by a single 6.4-eV photon of the ArF excimer laser.[3,4] While they are certainly present in the sublimed film in significant quantities, their actual relative abundance in the sublimed film compared to the two-photon-ionized $(@C_n)$ species may be as low as a few percent.

Although this stability of these lanthanum fullerenes is impressive, the fact that they were buried in a good quality C_{60}/C_{70} film means that most of them were never actually exposed to air. When they *were* exposed, a dramatic difference was seen. Figure 2 shows the FT-ICR spectrum of a sample probed in the same, gentle way. Except here the fullerenes were obtained by collecting the initial black-brown deposit in the quartz tube (which is easily brushed off of the tube surface, much like the raw soot from a standard carbon-arc fullerene synthesis). This black powder was then Soxhlet extracted for 2 h in boiling toluene. No attempt was made to exclude air or moisture. The resultant solution was then evaporated, and the extracted material redissolved (or, at least, resuspended) in a small amount of toluene so it could be deposited on a copper FT-ICR sample disk. Note that effectively the only lanthanum-containing fullerene to be extracted by hot toluene and survive exposure to Houston's mid-August weather was $(La@C_{82})$.

This stability and toluene extractability of $(La@C_{82})$ led us to suspect it could be made and recovered as well by the standard carbon arc technique now widely used to produce C_{60}, C_{70}, and the higher empty fullerenes. Accordingly two 1.25-cm-diameter graphite rods were bored out down the center axis of one end to form a 1.0-cm-diameter, 10-cm-long cavity. They were filled with a mixture of La_2O_3 (22%), graphite powder (45%), and pitch (33%). After being baked to carbonize the pitch, the rods were then used as opposing electrodes in our present scaled-up version of the carbon arc fullerene generator described in an earlier publication from this group.[9] Soot collected from this run was then Soxhlet extracted with toluene, the resulting fullerene solution concentrated down, and a small portion deposited on an FT-ICR sample disk. The resultant FT-ICR mass spectrum was similar to that shown in Figure 2: $(La@C_{82})$ was the only lanthanum fullerene detected. It appeared in substantially lower relative yield that the laser-vaporization sample of Figure 2, but we expect optimization of La_2O_3 loading levels in the graphite electrodes, more thorough carbonization, and adjustment of the operating conditions of the arc will enable $(La@C_{82})$ to be produced at yield levels similar to that of the most stable empty fullerene in this size region, C_{84}.

Such experiments with large amounts of heavy-metal oxides in carbon arcs should be done with caution. The oxides are readily reduced under conditions of the arc to the neutral metal, and there is no guarantee that all of these metal atoms will end up safely on the inside of carbon cages. In addition to their toxicity, finely dispersed lanthanum metal atoms on the *outside* of graphitic carbon structures are highly pyrophoric, as was demonstrated to us quite memorably when we vented the carbon arc apparatus rapidly to air after our first run. We now bleed in a small amount of air while the apparatus is still under vacuum, converting the surface lanthanum into La_2O_3 at a slow, controlled rate.

Why Is $(La@C_{82})$ Special?

This unique stability of a lanthanum-containing fullerene at 82 carbon atoms at first seems strange. For the normal, empty fullerenes the most abundant are usually 60, 70, 84, and to some extent 76, in decreasing order of apparent stability.[14] When probing sublimed or solvent-deposited C_n fullerene films with this FT-ICR apparatus, this relative abundance pattern is readily seen.

However, with an internal lanthanum atom, there ought to be a change in this pattern of stabilities. Calculations of the electronic structure of $(La@C_{60})$ have been done by Rosen and Wastenburg[15] and more recently by Chang et al.[16] The La is predicted (in the latest calculation) to donate both its 6s electrons into the delocalized aromatic shell system of the carbon cage, leaving behind a single 5d electron. In the case of C_{60} this pair of donated electrons can only go into the t_{1u} LUMO shell, producing a molecule whose reactivity should be like that of the triplet state[17] of normal C_{60}. Although the relevant calculations have not yet been done, it is likely that the same circumstance will apply to the other particularly stable empty fullerenes, C_{70}, C_{84}, and C_{76}, all of which are closed-shell ground-state singlets with substantial HOMO–LUMO gaps.

In view of the results of Figure 1, we suspect there is still a way that one can end up with a closed-shell fullerene with a lanthanum inside. If as in metal clusters such as K_x or Cu_x where the shell model works it is also true in these hollow-shell fullerenes that it is the electron count that matters most, then the stability of C_{84} means that 84 must be a stable shell closing. By dropping down to the C_{82} fullerene and adding two extra electrons from the 6s shell of an internal lanthanum atom, one regains the 84 electron count, and there may be an arrangement of the pentagons and hexagons that preserves this as a shell closing. The resultant

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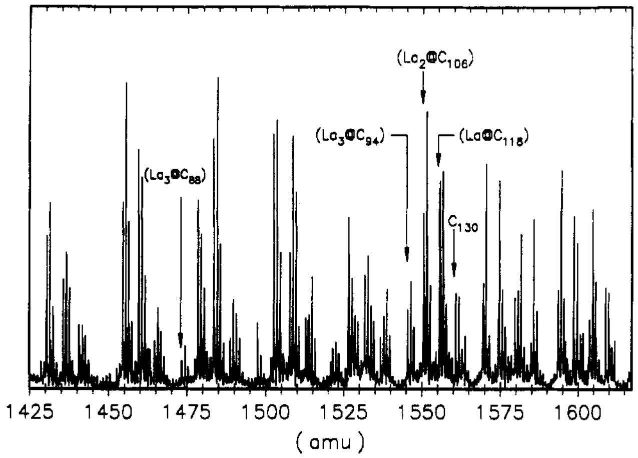

Figure 3. FT-ICR mass spectrum showing the existence of fullerenes with up to three lanthanum atoms trapped inside.

$(La@C_{82})$ would be a closed-shell singlet with a substantial HOMO–LUMO gap.

This would nicely explain $(La@C_{74})$ as being the next most stable lanthanum fullerene—it has the same 76-shell electron count as C_{76}. The lower panel of Figure 1 shows that $(La@C_{74})$ does appear to be nearly as abundant as $(La@C_{82})$ in the sublimed film. But no such trick can be found at the 60- and 70-electron shell closings since $(La@C_{58})$ and $(La@C_{68})$ have no structures that avoid adjacent pentagons.

It will be interesting to see if these simple ideas hold up to detailed calculations. But, regardless of these speculations, it is clear that in reality $(La@C_{82})$ truly is special.

Metallofullerene Coalescence: More Atoms Inside. In the course of this work we were interested in finding what levels of vaporization laser fluence were capable of producing $(La@C_n)$ fullerenes from the La_2O_3/graphite composite and whether there were any conditions that would give FT-ICR mass spectra similar to those of Figure 1 even though the metallofullerenes did not originally exist on the FT-ICR sample disk. We found that laser vaporization of a 0.1-cm-thick disk of the same La_2O_3/graphite rod used to generate the sublimed film sample of Figure 1 did not produce any detectable fullerene signal when probed in the FT-ICR cluster source with desorption laser fluences less than 1 mJ. However, when struck with vaporization laser pulses of >10 mJ, this composite disk did produce readily detectable fullerene and metallofullerene signals in the FT-ICR apparatus. Quite unlike in Figure 1, these cluster distributions were extremely broad, with only slight evidence for special stability of clusters such as C_{60}, $(La@C_{60})$, and $(La@C_{82})$.

The most interesting result, however, concerned the time development of the cluster FT-ICR mass spectrum. Initially, as the vaporization laser struck fresh surfaces of the composite sample, the cluster distribution was primarily made up of C_n clusters with $n < 60$, with only a small amount of $(La@C_n)$ lanthanum fullerenes evident. As the target disk was moved around for the second pass, the cluster signal became more intense, extended out to clusters well over 100 atoms in size, and was dominated by $(La@C_n)$. Further laser blasting of the composite disk continued to change the cluster distribution, showing strong signals for clusters of composition La_2C_n and even La_3C_n. Figure 3, for example, shows a portion of the FT-ICR cluster mass spectrum obtained after extensive laser-aging of the composite target disk. Signals due to La_3C_n clusters are seen here to grow in importance as a function of cluster size, starting with La_3C_{88}.

In a series of XeCl excimer laser photofragmentation and reaction tests with O_2 and ammonia reactants, we were able to prove that all these clusters were, in fact, $(La_x@C_n)$ lanthanum fullerenes. As levitated positive ions in the FT-ICR apparatus, they are chemically inert, and they fragment only by successive C_2 losses. Laser "shrink wrapping" experiments showed that the smallest cage that can surround two lanthanum atoms is C_{66}, and the minimum cage that can fit around three is C_{88}.

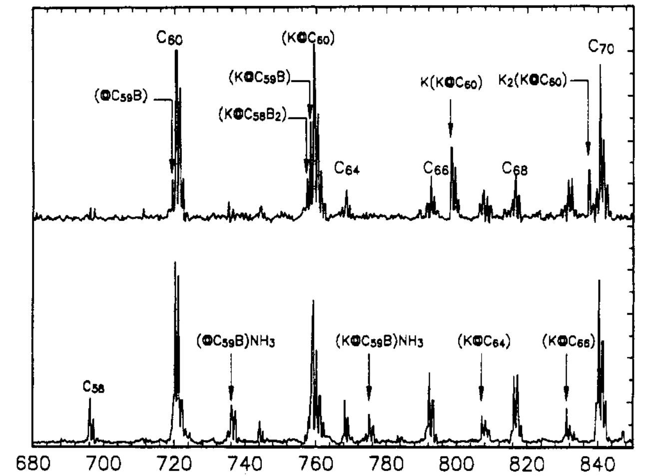

Figure 4. FT-ICR mass spectra showing evidence for the production of boron and boron/potassium doped 60-atom fullerenes. The bottom panel shows the result of reaction with ammonia. Note that the boron-doped clusters have been titrated with ammonia, demonstrating that the boron is substituting for a carbon as part of the fullerene cage. Note also that the clusters in the top panel marked $K(K@C_{60})^+$ and $K_2(K@C_{60})^+$ are missing after reaction with ammonia in the bottom panel, demonstrating that the extra potassium atoms were on the outside, unprotected by the fullerene cage.

The mechanism for formation of these clusters is unknown, but from the observed dependence on laser aging the target surface, we suspect they are generated by $(La@C_n)$–$(La@C_n)$ coalescence reactions occurring either on the target disk surface or in the laser-induced plasma just above this surface. Detailed probes of such laser-zapped metal/graphite surfaces by STM and various types of photoemission may be quite fascinating.

We note in passing that the recent transmission electron microscopy pictures of C_{60} films by Wang and Buseck[19] show evidence of C_{60}–C_{60} coalescence to form cylindrical "bucky tubes" in the solid film, presumably triggered by the 400-keV electron beam. We wonder if metal atom encapsulation events would occur under similar circumstances with metal-doped fullerene films.

Potassium/Boron Doped Fullerenes. In an attempt to produce boron-doped fullerenes[20] using a boron/graphite composite target rod in the 1200 °C tube furnace, we produced a material that when sublimed onto a sample disk gave the FT-ICR mass spectra shown in Figure 4. The top panel shows excellent evidence for the existence in this sublimed fullerene film of not only $(@C_{59}B)$ but also $(K@C_{60})$, $(K@C_{59}B)$, and $(K@C_{58}B_2)$. The potassium had been introduced by accident since at the time the experiment was done the only quartz tube that was available was a dirty one that had been used months before to produce a KCl/graphite composite rod. It still had KCl deposited on the inner surfaces of the tube, baked in so effectively that it could not be removed. The bottom panel shows the resultant FT-ICR mass spectrum after exposure to ammonia reactant gas. The boron-doped fullerenes here are seen largely titrated with ammonia. Note also that the signals labeled in the top panel as $K(K@C_{60})$ and $K_2(K@C_{60})$ are missing after reaction with ammonia. They are outside complexes, $K_x(K@C_{60})^+$, which react with NH_3 to produce (we suspect) $K_{x-1}(K@C60)$ and KNH_3^+. XeCl excimer laser photolysis of the $(K@C_{60})^+$, $(K@C_{59}B)^+$, and $(K@C_{58}B_2)^+$ clusters shows only successive C_2 losses, demonstrating that they have the single potassium atom safely doped on the inside.

Conclusion

Experiments such as those discussed above have led us to suspect there will soon be a vast new array of doped fullerene species generated by both laser-vaporization and arc techniques. The method used here involving laser vaporization in a tube furnace,

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followed by sublimation onto a substrate, has the advantage that even rather reactive open-shell doped fullerenes can be stabilized by embedding in a C_{60}/C_{70} matrix. This matrix is of sufficient quality to permit the film to be exposed to air for substantial periods of time. Subsequent dissolution of these fullerene films in appropriate solvents in air- and water-free environment should permit the more reactive doped fullerenes to be separated and passivated by attachment of protecting groups, or by formation of stable salts or complexes.

Acknowledgment. The delightful suggestion of the use of the @ symbol in formulas for complex fullerenes is due to Ori Cheshnovsky. We thank Lai-Sheng Wang, Jose Conceicao, and Lila Anderson for help and encouragement in the early, fitful beginnings of this work on "dopyballs". This research was supported by the National Science Foundation, the Office of Naval Research, and the Robert A. Welch Foundation, using a cluster FT-ICR apparatus developed with major support from the U.S. Department of Energy, Division of Chemical Sciences.

Dichroism in Solutions of C_{70} in Nematic Hosts

M. A. Marcus,* R. C. Haddon, A. V. Makhija, S. F. Zahurak, and A. R. Kortan

AT&T Bell Labs, 600 Mountain Avenue, Murray Hill, New Jersey 07974 *(Received: June 13, 1991)*

We measured the optical absorption and dichroism of parallel-aligned samples of solutions of C_{70} and C_{60} in nematic hosts. We find that the solutions of C_{70} show considerable dichroism, which we attribute to the nonspherical shape of the C_{70} molecule. The optical absorption with the $\vec{E}$ vector parallel to the nematic director is greater than that with $\vec{E}$ perpendicular to the director for wavelengths between 380 and 425 nm. The sign is reversed above 425 nm.

Introduction

The discovery by Krätschmer et al.[1] of a method for producing fullerenes in bulk quantities has caused an intense flurry of interest and experiment in the cluster community. Due to its large relative abundance in the carbon soot made by this process, the C_{60} species has attracted the most attention. It is now fairly well established that C_{60} is indeed the long-sought "buckyball".[2-7] However, the evidence for the structure of C_{70} is not yet as solid as for C_{60}. In particular, the predicted structure for C_{70} is a prolate ellipsoid,[8] whereas no direct evidence for a nonspherical shape has yet turned up.

If a molecule of symmetry lower than cubic is placed in an oriented nematic liquid crystal, the guest molecule will take on some of the orientational ordering of the host.[9] The resulting solution will then be dichroic, since the strengths of the molecular absorption bands will depend on the angle between the transition dipole and the incident polarization. Thus, long, conjugated molecules are used as dyes in guest-host displays because they are much more absorbing when the nematic director is parallel to the $\vec{E}$ field than otherwise.

Therefore, we did a comparison of the dichroism of solutions of C_{70} and C_{60} in nematic solvents in order to see whether C_{70} is nonspherical and perhaps to help assign some of the optical absorption bands.

Experimental Section

C_{60} and C_{70} were isolated from crude soot extract made in an arc melter by chromatography.[10]

The liquid crystals used were 4-pentyl-4′-cyanobiphenyl (5CB) and a commercial biphenyl-based mixture (E9), both from EM Industries. The fullerenes were dissolved in the host compounds either directly or by dissolving both components in toluene, which was evaporated off. Concentrations used ranged from 0.09 to 0.4 wt %. The solubility of both fullerenes in the hosts was about 0.2%, so the 0.4% solution was metastable and formed precipitates, leaving a saturated solution.

The solutions were loaded into flat cells made of surface-treated glass plates separated by spacers and epoxied together. Most of the plates were treated by washing in Alconox detergent, rinsing, drying, and rubbing with paper towels. This crude treatment resulted in acceptable alignment over areas large enough for measurement. One pair of cells was made with a rubbed polyimide surface coating, leading to excellent alignment. The results were independent of the surface treatment used.

Optical absorption measurements were made with a Hewlett-Packard 8452A diode-array UV-vis spectrometer. A Nicol prism was inserted in the light path for dichroism measurements. This instrument is a single-beam machine, so a measured spectrum actually consists of the logarithm of the ratio of the intensity transmitted through the sample to that for the blank. For dichroism measurements, "sample" and "blank" are the same sample, oriented with the director parallel and perpendicular to the $\vec{E}$ vector, respectively. This instrument can detect changes in optical absorption of 0.01OD or less. To measure the absorption due to the fullerene alone, we used a cell filled with undoped liquid crystal for the blank and made sure that the two samples were run in the same orientation.

Results

The optical absorption of a 0.09 wt % C_{70} solution in E9 (24-μm path length) is shown in Figure 1a,b for polarization parallel and perpendicular to the nematic director. In each case, we have subtracted off the absorption from an undoped sample of E9 in the same polarization. This procedure thus yields the absorption

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