

## PRODUCTION AND CHARACTERIZATION OF METAL-ENCAPSULATED FULLERENES

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### ABSTRACT

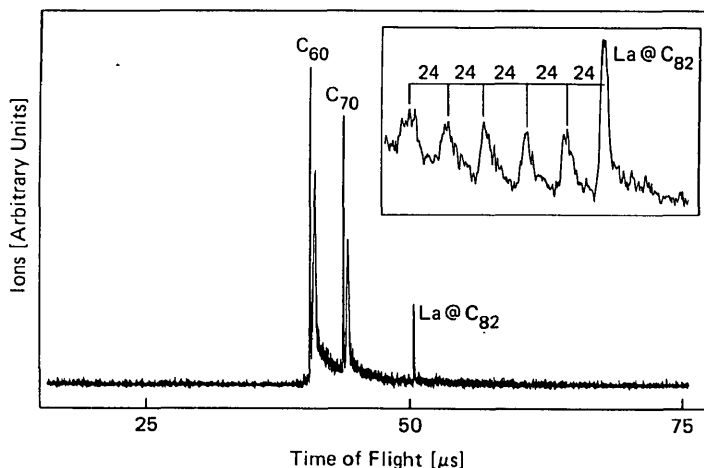
We report here the arc-production and spectroscopic characterization of fullerene-encapsulated metal atoms and metal-atom clusters. In particular, both solution and solid-state electron paramagnetic resonance (EPR) spectra of  $\text{LaC}_{82}$ ,  $\text{YC}_{82}$ ,  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$  have been obtained. Additional species containing rare-earth atoms and clusters have been produced. The results suggest, for example, that the three scandium atoms in  $\text{Sc}_3\text{C}_{82}$  form a molecule in the shape of an equilateral triangle — as was previously suggested for  $\text{Sc}_3$  molecules isolated in a cryogenic rare-gas matrix. The spectra of the  $\text{MC}_{82}$  species ( $M=\text{La}, \text{Y}, \text{Sc}$ ) exhibit small hyperfine couplings and g-values close to 2, suggesting that they can be described as a +3 metal cations within — 3 fullerene radical anion cages.  $\text{Sc}_2\text{C}_{2n}$  species — the most abundant metallofullerenes in the scandium-fullerene mass spectrum — are EPR-silent, even though  $\text{Sc}_2$  is EPR-active in a rare-gas matrix at 4.2K. A broader implication of this work is that production of macroscopic quantities of metal-containing fullerenes may make possible the fabrication of exotic new structures with regular arrays of metal atoms or clusters isolated in fullerene molecules, resulting in new types of host/guest nanostructured materials.

The bulk production of fullerenes with entrapped atoms or clusters has been a vigorously pursued goal since the advent of the Krätschmer-Huffman technique for producing hollow fullerenes.<sup>1, 2</sup> Elegant carbon cluster-beam experiments using metal-impregnated graphite,<sup>3-6</sup> which began very soon after the fullerene structures for large carbon clusters were first proposed,<sup>7</sup> had already provided convincing evidence that endohedral metallofullerenes can be produced — at least as transients. More recently, the chemical stability reported for  $\text{LaC}_{82}$ ,<sup>8, 9</sup>  $\text{La}_2\text{C}_{80}$ ,<sup>10</sup>  $\text{YC}_{82}$ ,  $\text{Y}_2\text{C}_{82}$ ,<sup>11, 12</sup>  $\text{ScC}_{82}$ ,  $\text{Sc}_2\text{C}_{2n}$ ,  $\text{Sc}_3\text{C}_{82}$ <sup>13, 14</sup> and  $\text{FeC}_{60}$ <sup>15</sup> in solution and in the solid state, has given new impetus to efforts to produce purified bulk quantities of fullerenes with metal atoms and clusters entrapped within the cages. These novel fullerene variants could be the basis of a new class of materials with arrays of metal atoms or clusters isolated, stabilized, and held in position by a lattice of surrounding carbon shells. Fullerene encapsulation also provides a novel method for isolating and stabilizing reactive species under ambient conditions, opening up the possibility of examining them spectroscopically to learn about their detailed structure.

Following the success reported by Chai et al.<sup>8</sup> in producing lanthanum-containing fullerenes, both by laser vaporization of metal-containing graphite and by arc-burning a graphite/lanthanum-oxide composite bar, we prepared lanthanum fullerenes using a variation of their reported arc procedure. In our case, graphite and  $\text{La}_2\text{O}_3$  were mixed with a binder (dextrin), partially dried, and pressed into a rod. After caramelizing at  $150^\circ\text{C}$ , the rod was heated to  $1400^\circ\text{C}$  for 2 hours. The soot produced by arc-vaporization of the rod under 200 Torr He was extracted with toluene, and the extract was washed with diethylether and dried. The resulting powder was analyzed using mass spectrometry and ESR spectroscopy.<sup>9</sup>

Figure 1 shows the time-of-flight mass spectrum of material laser desorbed from the dry powder. Large peaks for  $\text{C}_{60}$ ,  $\text{C}_{70}$  and  $\text{LaC}_{82}$  are the dominant features. The inset in Fig. 1 shows the fragmentation pattern found for  $\text{LaC}_{82}$  when the ionization laser (193 nm) intensity was increased. This pattern is consistent with the pair-wise removal of carbons from the skeletal cage, with the La atom remaining inside the resulting smaller fullerene.<sup>4</sup> The two groups of peaks centered about 15 mass units above the  $\text{C}_{60}$  and  $\text{C}_{70}$  peaks are due to 25%  $^{13}\text{C}$ -enriched  $\text{C}_{60}$  and  $\text{C}_{70}$  left over in the arc chamber from an earlier burn and inadvertently vacuumed up along with the material produced for this experiment. They serve the useful purpose of demonstrating that the observed  $\text{LaC}_{82}$  is *not* formed from  $\text{C}_{60}$  or  $\text{C}_{70}$  and lanthanum in the course of the laser-desorption/laser-ionization mass spectrometry, but was present in the original toluene extract of the soot.<sup>16</sup>

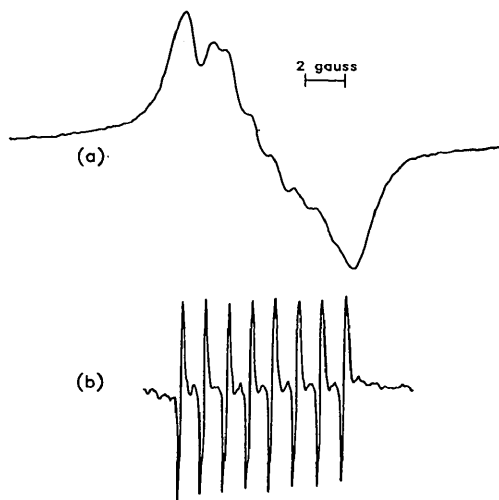
**Figure 1.** Mass spectrum of toluene extract of soot from arc burning a composite graphite/ $\text{La}_2\text{O}_3$  rod. Inset shows how  $\text{La@C}_{82}$  loses even numbers of carbons at high ionization intensities.



As La has three valence electrons, the endohedral complex was expected to show paramagnetism, and EPR spectroscopy proved to be a useful probe of the electronic state of the  $\text{LaC}_{82}$  complex. The EPR spectrum of the solid powder is shown in Figure 2a. A structured EPR spectrum is observed, centered at  $g = 2.001$ ,

with a relatively narrow width of 10 gauss; this indicates the presence of an unpaired electron. The spectrum sharpens dramatically upon dissolving this material in 1,1,2,2-tetrachloroethane: an eight line pattern is observed, consisting of extremely narrow resonances (0.125 gauss), with a uniform separation of 1.25 gauss. The eight line pattern is diagnostic of hyperfine coupling (hfc) to a nuclear spin of  $7/2$ , which is the spin of the 100% abundant  $^{139}\text{La}$  nucleus. This coupling indicates unpaired electron density on the La nucleus. The observed hfc of 1.25 gauss is very small. The hfc measured for  $\text{La}^{+2}$  in a  $\text{CaF}_2$  lattice is  $\sim 50$  gauss<sup>17</sup>, and a calculation for  $\text{La}^{+2}$  using spin-polarized unrestricted Hartree-Fock wave functions yielded an hfc of 186 gauss. We therefore conclude that the valence state of the La metal atom is  $+3$ . This is consistent with calculations of the electronic structure of  $\text{LaC}_{60}$ , which found a  $+3$  charge for the lanthanum atom in that species.<sup>18</sup> Fig. 2b shows that there is an intensity maximum between each La line. Since 60% of the  $\text{LaC}_{82}$  moieties will contain at least one  $^{13}\text{C}$ , this intensity is consistent with hyperfine coupling to  $^{13}\text{C}$  in natural abundance; the spectrum is expected to be broadened due to the large number of inequivalent carbons in a  $\text{C}_{82}$  cage. The observation of coupled electron,  $^{139}\text{La}$  and  $^{13}\text{C}$  spins provides direct evidence for the association of a La atom with the  $\text{C}_{82}$  framework.

An interesting observation is that EPR spectra of toluene solutions of the toluene extract from the La-soot show a second overlapping octet of lines, with  $g = 1.9989$  and a hfc of 0.83 gauss, corresponding to a second single lanthanum fullerene species.<sup>19</sup> Mass spectrometry of a deposit of this sample indicates that  $\text{LaC}_{82}$  is the only metallofullerene present, suggesting that two different conformers of this species may be responsible for the two EPR spectra, and that the solvent can influence their populations.

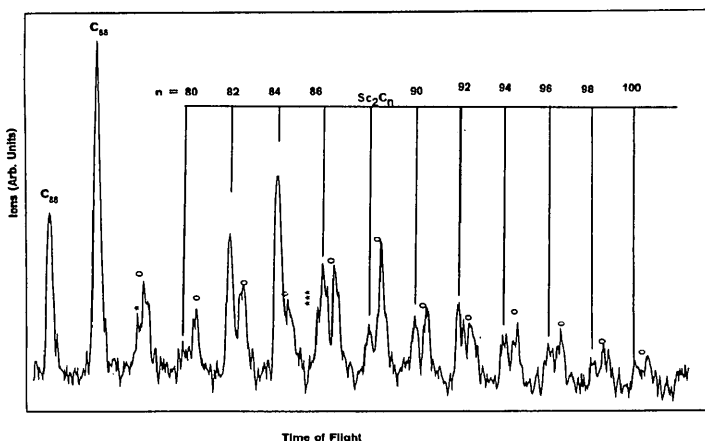


**Figure 2.** EPR spectra (9.5112 GHz) at ambient temperature of: (a) solid toluene extract (dried and degassed) of soot produced by arc burning a composite graphite/ $\text{La}_2\text{O}_3$  rod and (b) a degassed solution of the same extract in 1,1,2,2-tetrachloroethane.

After our initial work with  $\text{La}_2\text{O}_3$  composite rods, we developed an alternative scheme to conveniently produce metallofullerenes using pure powdered metals rather than oxides. 6 mm graphite rods were drilled out to give a 4 mm id x 50 mm cavity which was filled (under an argon atmosphere) with a mixture of metal and graphite powders. The overall metal/carbon ratios were in the range 1-2% (atomic). The tamped powder was retained by a short threaded graphite plug. These rods were arc-burned under He (200 Torr). Using this method lanthanum, yttrium, scandium, and various lanthanide containing fullerenes were produced and characterized by mass spectrometry and EPR.<sup>19</sup>  $\text{YC}_{82}$  was found to be the dominant single-metal metallofullerene in toluene extract, and gave an EPR spectrum similar to that reported by Weaver et al.<sup>11</sup> and Shinohara et al.<sup>12</sup>, who observed a doublet centered at  $g=1.9999$  and  $g=2.00013$ , respectively, with a hyperfine coupling of only 0.48 gauss. This small hyperfine coupling, and the XPS spectrum obtained for a sublimed film containing  $\text{YC}_{82}$  by Weaver et al. lead to the conclusion that, as in the case of lanthanum, the valence state of the yttrium atom is +3. In EPR spectra of toluene solutions of toluene extract of the yttrium soot, we find a second doublet with  $g=1.9993$  and  $A=0.375$  gauss. The similarity of this pattern of two spectra to the lanthanum case is striking, and is likely to have an analogous origin. Species such as  $\text{Y}_2\text{C}_{2n}$ , which are abundant in toluene extracts of yttrium metallofullerenes,<sup>11, 12</sup> give no clear EPR spectra, suggesting that they may be diamagnetic.

The case of scandium metallofullerenes<sup>13, 14</sup> is particularly interesting, since the smaller ionic radii of scandium apparently favors the production of multi-metal metallofullerenes. As shown in Figure 3, the most prominent metallofullerenes found in a toluene extract of the arc soot are  $\text{Sc}_2\text{C}_{2n}$  with  $80 \leq 2n \leq 100$ . The most abundant single and triple metal-atom containing fullerenes present are  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$ .

**Figure 3. Mass spectrum of toluene extract of scandium-metallofullerene soot, showing the dominant  $\text{Sc}_2\text{C}_{2n}$  series. The single and triple asterisks indicate  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$ , respectively. Empty fullerenes in the range  $2n=90-112$  are marked by zeroes.**

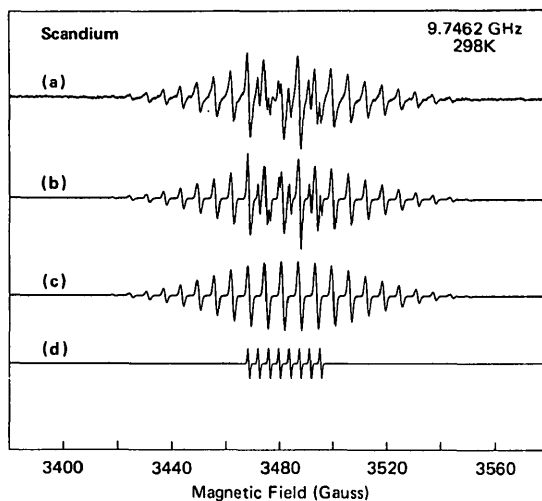


The room-temperature EPR spectrum of such a solution is shown in Figure 1a. Qualitatively, the spectrum appears to be the superposition of two spectra centered around  $g = 2$ , one consisting of 8 equally-spaced lines of roughly equal intensity and the other a symmetrical pattern of 22 lines, with intensities decreasing monotonically outward from the spectral center. We have been able to simulate the experimental spectrum by superposing simulated EPR spectra with isotropic electron-nuclear hyperfine coupling in species which contain (1) *three equivalent scandium nuclei* (Fig. 1c) and (2) a single scandium nuclear spin (Fig. 1d) -  $^{45}\text{Sc}$  is 100% abundant with a nuclear spin of  $7/2$ . The spectrum with hyperfine coupling to a single scandium nucleus consists of eight equally-spaced lines with equal intensity, while the three-spin simulation generates 22 lines with relative intensities

1:3:6:10:15:21:28:36:42:46:48:48:46:42:36:28:21:15:10:6:3:1.

The superposition of Figs. 1c and 1d yields the simulation shown in Fig. 1b, in excellent agreement with experiment (Fig. 1a), suggesting that the EPR spectrum is due to just two species which we tentatively identify as  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$ . The simulation for  $\text{Sc}_3\text{C}_{82}$  (Fig. 1c) has a hyperfine coupling of 6.22 gauss and is

**Figure 4.** a) EPR spectrum of a room-temperature toluene solution containing scandium metallofullerenes; b) superposition of two simulated spectra arising from for an unpaired electron spin coupled to (c) three equivalent scandium nuclei and (d) a single scandium nucleus.



centered at  $g = 1.9985$ . This  $g$  value is close to that for  $\text{LaC}_{82}^9$  (2.0010) and the  $\text{C}_{60}$  radical anion.<sup>20-23</sup> The EPR spectrum of  $\text{Sc}_3$  has been observed in an argon matrix

at 4K and could be simulated using a near-isotropic  $g$  tensor (1.9933) and an axially symmetric hyperfine tensor with  $A_{\parallel} = 25.52$  gauss and  $A_{\perp} \cong 0$ , corresponding to an isotropic hyperfine splitting of 8.51 gauss.<sup>24</sup> The  $g$  value found in the rare-gas matrix is somewhat lower than for the  $\text{Sc}_3\text{C}_{82}$ , while the isotropic hyperfine coupling is slightly larger. On the basis of these results we propose that the three equivalent scandium atoms form a  $\text{Sc}_3$  molecule in a doublet ground state with the geometry of an equilateral triangle – conclusions similar to those reached for  $\text{Sc}_3$  in a cryogenic matrix environment (also on the basis of EPR spectroscopy).<sup>25</sup>

The  $g$  value for  $\text{ScC}_{82}$  is 1.9998, quite close to the values for  $\text{Sc}_3\text{C}_{82}$ ,  $\text{LaC}_{82}$ ,  $\text{YC}_{82}$  and the  $\text{C}_{60}$  radical anion. The hyperfine coupling in  $\text{ScC}_{82}$  (3.82 gauss) is smaller than for the  $\text{Sc}_3$  species, but is about three times larger than the coupling measured for  $\text{LaC}_{82}$  (1.25 gauss).<sup>9</sup> We calculated the hyperfine coupling for  $\text{Sc}^{+2}$  using unrestricted Hartree-Fock wave functions, and obtained a value of -120 gauss, considerably larger than the measured value. On the basis of this difference, we propose that the scandium atom is in the +3 oxidation state, and that the structure is  $\text{Sc}^{+3}\text{C}_{82}^{-3}$ . Similar conclusions were drawn from EPR spectra of the corresponding lanthanum complex,  $\text{La}^{+3}\text{C}_{82}^{-3}$ .<sup>9</sup> However, the larger hyperfine coupling in the scandium case suggests that the electron spin may be more closely associated with the scandium atom in  $\text{ScC}_{82}$  than it is with the lanthanum atom in  $\text{LaC}_{82}$ .

The absence of other resonances, searched for at temperatures ranging from 4.2K to ambient over a wide range of magnetic field strengths (0 to 0.6T), suggests that the  $\text{Sc}_2\text{C}_{2n}$  species (predominant relative to Sc and  $\text{Sc}_3$  species in mass spectra) are diamagnetic. Since Knight and co-workers have detected an EPR spectrum for  $\text{Sc}_2$  in rare-gas matrices at 4.2K, our results suggest that the scandium valence electrons in  $\text{Sc}_2\text{C}_{82}$  are paired, either in the metal dimer orbitals, or in LUMO's in the fullerene cage. Very similar results for metallofullerenes with 1, 2 or 3 scandium atoms have recently been obtained by Shinohara et al.<sup>14</sup>

Production of macroscopic quantities of cluster-containing fullerenes has made it possible to obtain the first detailed information about the structure of metallofullerenes using EPR spectroscopy. In the near future it may make possible the fabrication of exotic new structures with regular arrays of metal-atom clusters isolated in fullerene molecules resulting in a new type of host/guest nanostructured material.<sup>26</sup> The realization of such materials depends on the development of methods for separation, purification, and crystallization -- in short all of the steps which have been successfully carried out for empty fullerenes such as  $\text{C}_{60}$ . Efforts to accomplish these steps are underway at a number of laboratories worldwide.

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