

## Metal Atoms and Clusters in Fullerene Cages

Donald S. Bethune, Costantino S. Yannoni, Mark Hoinkis, Mattanjah de Vries,  
Jesse R. Salem, Mark S. Crowder\* and Robert D. Johnson

IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099

\*IBM Adstar, 5600 Cottle Rd., San Jose, CA 95193

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**Abstract.** Fullerenes containing metal atoms and clusters can be formed by the arc-vaporization method. The electronic structure of these metallofullerenes can be probed using magnetic resonance techniques. 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. Metallofullerenes containing a single metal atom ( $\text{MC}_{82}$  with  $M = \text{La}, \text{Y}, \text{or Sc}$ ), have small hyperfine couplings and  $g$ -values close to 2, implying that they can be described as +3 metal cations within -3 fullerene radical anion cages. In the La and Y cases, additional EPR active  $\text{MC}_{82}$  species have been found. The EPR spectrum of  $\text{Sc}_3\text{C}_{82}$  shows that the metal atoms are equivalent, suggesting that they may form a triangular molecule. No EPR spectrum is found for  $\text{Y}_2\text{C}_{82}$  or for  $\text{Sc}_2\text{C}_{2n}$  species (with  $2n = 82, 84, 86$ ), suggesting that they are diamagnetic. Sc NMR spectra of a solution containing  $\text{Sc}_2\text{C}_{2n}$  species have been obtained which confirm the diamagnetism of the scandium metallofullerenes.

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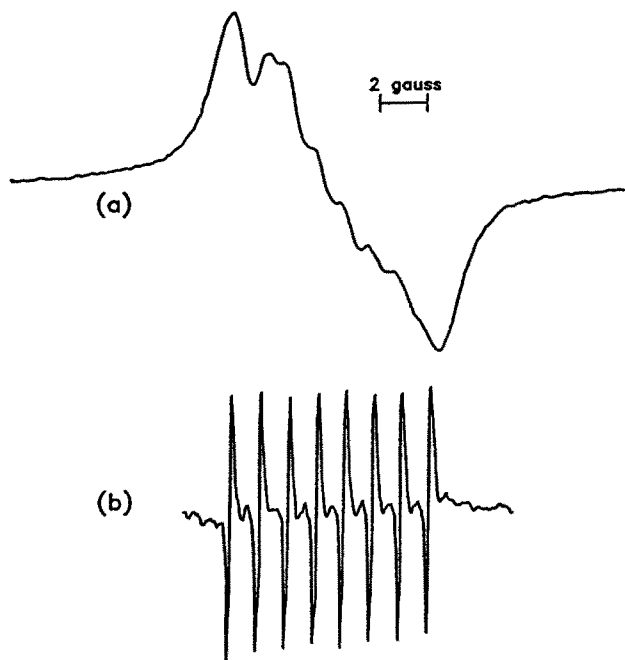
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At the time that the fullerene structures were proposed for large carbon clusters<sup>1</sup> on the basis of carbon cluster beam experiments,<sup>1, 2</sup> it was pointed out that the 4Å diameter cavity inside the  $\text{C}_{60}$  cage was large enough to allow any atom and many small molecules to be trapped inside.<sup>1</sup> Experimental evidence that this idea could be realized was soon provided by carbon cluster-beam experiments based on laser ablation of metal-

impregnated graphite.<sup>3-6</sup> Such species would be an interesting new class of molecules, with tunable electronic, optical, vibrational and chemical properties; they could topologically bond carbon with species which would normally be considered inert, and they could allow refractory materials to be put into gas phase at much lower temperatures. They could also be the basis of a new class of materials, with electronic and optical properties which could be tuned by placing various atoms, molecules or clusters inside the carbon cages of a fullerene crystal.

The breakthrough development of a simple technique for mass producing fullerenes by Krätschmer et al.<sup>7, 8</sup> inspired new efforts to produce metallofullerenes in macroscopic quantities. After the initial success of Chai et al.<sup>9</sup> in producing lanthanum-containing fullerenes, both by laser-vaporization of metal-containing graphite and in trace amounts by arc-burning a graphite/ $\text{La}_2\text{O}_3$  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°C, the rod was heated to 1400°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. As La has three valence electrons, any neutral complex of La with a fullerene must have an odd electron count and thus will be paramagnetic. EPR

spectroscopy was therefore tried on the toluene extract of the La containing soot.<sup>10</sup> The EPR spectrum of the solid powder is shown in Figure 1a. A relatively narrow (10 gauss) structured resonance is found, centered at  $g = 2.001$ , confirming the presence of species with an unpaired electron. The mass spectrum of this sample showed only a single metallofullerene:  $\text{LaC}_{82}$ .

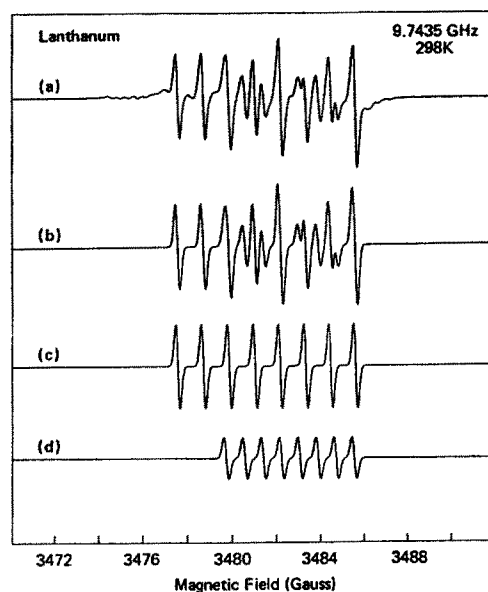


**Figure 1.** EPR spectra (9.5112 GHz) at ambient temperature of: (a) solid toluene extract (dried and degassed) of soot produced by arc burning a composite graphite/ $\text{La}_2\text{O}_3$  rod and (b) a degassed solution of the same extract in 1,1,2,2-tetrachloroethane (TCE).

When this material was dissolved in 1,1,2,2-tetrachloroethane (TCE), the spectrum sharpened dramatically, as seen in Figure 1b. The eight line pattern consists of extremely narrow resonances (0.125 gauss), uniformly spaced 1.15 gauss apart. This pattern is diagnostic of hyperfine coupling (hfc) to a nucleus with spin  $7/2$ , specifically the 100% abundant  $^{139}\text{La}$  nucleus. The observed hfc of 1.15 gauss is very small. In contrast,  $\text{La}^{+2}$  in a  $\text{CaF}_2$  lattice has a measured hfc of  $\sim 50$  gauss,<sup>11</sup> and a calculation for  $\text{La}^{+2}$  using spin-polarized unrestricted Hartree-Fock wave functions yielded an hfc of 186 gauss. These comparisons imply that the va-

lence state of the La atom is +3. This is consistent with early calculations of the electronic structure of  $\text{LaC}_{60}$ , which found a +3 charge for the lanthanum atom in that species.<sup>12</sup> More recent electronic structure calculations,<sup>13</sup> which assume a  $\text{C}_{3v}$  structure for the  $\text{C}_{82}$  cage,<sup>14</sup> show that the question of the valence expected for the La atom is subtle: if the atom is held at the center of the cage, it has a valence of +2. If the geometry is relaxed, the atom moves off the 3-fold axis by  $1.6\text{\AA}$  into a 4 eV deep well against the carbon shell, and assumes a valence of +3, in agreement with the EPR result.<sup>10</sup> This structure is quite polar. Fig. 1b also shows intensity maxima between each La line, consistent with hyperfine coupling to  $^{13}\text{C}$  nuclei, providing further evidence for the association of a La atom with a fullerene.

We were surprised to find that EPR spectra of TCE and toluene solutions of the toluene extract of a La-soot are distinctly different. The latter, shown in Figure 2a, in addition to an octet similar to that in Fig. 1b, has 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>15-17</sup>



**Figure 2.** EPR spectra (9.74 GHz) at ambient temperature of: (a) a toluene solution of toluene fullerene extract of soot produced by arc burning La containing carbon rods. (b) a superposition of two simulated spectra shown in (c) and (d).

Mass spectrometry shows that  $\text{LaC}_{82}$  is the only metallofullerene present in significant amount, implying that two isomers of this formula with markedly different chemical behavior are present in the sample.

After our initial La experiments, we began to make metallofullerenes by packing a loose mixture pure metal and graphite powders into a 6 mm diameter rod which had been bored out to 4 mm inside diameter to a depth of 5 cm. The filling operation was carried out under an Ar atmosphere and a short threaded graphite plug confined the powder. Overall metal/carbon ratios in the range 0.5-2% (atomic) have been used, and metallofullerenes containing La, Y, Sc, and various lanthanides have been produced by arc-burning such rods in a He atmosphere at 150-200 Torr.<sup>15</sup> With yttrium, for example,  $\text{YC}_{82}$  and  $\text{Y}_2\text{C}_{82}$  were the most abundant metallofullerenes in a toluene extract. EPR spectra of toluene solutions of this extract showed two doublets centered at  $g=2.0003$  and  $1.9998$ , with hfc's of 0.48 and 0.364 gauss, respectively, as also reported by Suzuki et al.<sup>17</sup> Weaver et al.<sup>18</sup> and Shinohara et al.<sup>19</sup> previously reported a single doublet for  $\text{YC}_{82}$  (centered at  $g=1.9999$  or  $g=2.00013$ , respectively) with a hyperfine coupling of 0.48 gauss. Again, the small hyperfine coupling and the XPS spectrum obtained for a sublimed film containing  $\text{YC}_{82}$ <sup>18</sup> lead to the conclusion that the metal valence state is +3. The similar patterns of two EPR spectra for  $\text{YC}_{82}$  and  $\text{LaC}_{82}$  suggests that analogous pairs of species are being produced using these metals. The fact that  $\text{Y}_2\text{C}_{82}$  is abundant in toluene extracts of yttrium metallofullerenes but shows no detectable EPR spectrum suggests that either it has very broad EPR lines or it is diamagnetic.

Besides  $\text{Y}_2\text{C}_{82}$ , other multi-atom metallofullerenes have been found to be stable and soluble in toluene and  $\text{CS}_2$ , including  $\text{La}_2\text{C}_{80}$ ,<sup>20, 21</sup>  $\text{Sc}_2\text{C}_{2n}$  and  $\text{Sc}_3\text{C}_{82}$ ,<sup>22, 23</sup> several rare earth metallofullerenes,<sup>15, 24</sup> and recently,  $\text{U}_2\text{C}_{2n}$ .<sup>25</sup> For Er samples made with nearly 2% metal in the rods, we found that  $\text{Er}_2\text{C}_{82}$  and

$\text{ErC}_{82}$  were the first and second most abundant metallofullerenes, with all others far less prevalent.

The case of scandium metallofullerenes<sup>22, 23</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  $2n = 82, 84, \text{ and } 86$ . The most abundant single and triple metal-atom containing fullerenes present are  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$ .

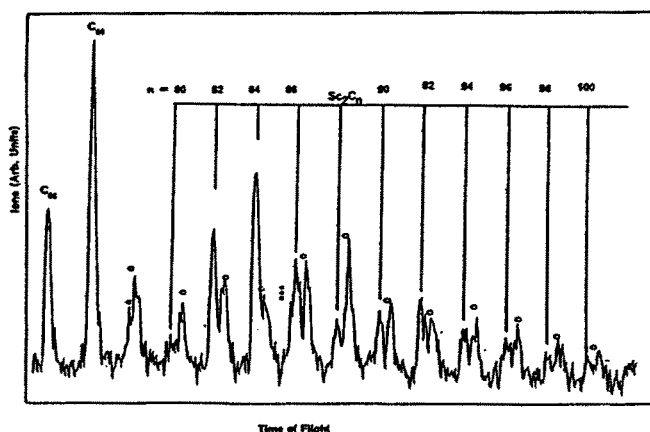


Figure 3. Mass spectrum of toluene extract of scandium-metallofullerene soot. The single and triple asterisks indicate  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$ , respectively. Empty fullerenes in the range  $2n = 90-112$  are marked by zeroes.

The room-temperature EPR spectrum of a solution of this extract is shown in Figure 4a. 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. The experimental spectrum can be simulated by superposing two EPR spectra with isotropic electron-nuclear hyperfine coupling in species which contain (1) *three equivalent scandium nuclei* (Fig. 4c) and (2) a single scandium nuclear spin (Fig. 4d).  $^{45}\text{Sc}$  is 100% abundant with a nuclear spin of  $7/2$ , so again the hfc of an

electron to a single scandium nucleus gives a spectrum with eight equally-spaced lines with equal intensity. Coupling an electron to three equivalent  $7/2$  spins gives a 22 line spectrum with relative intensities

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

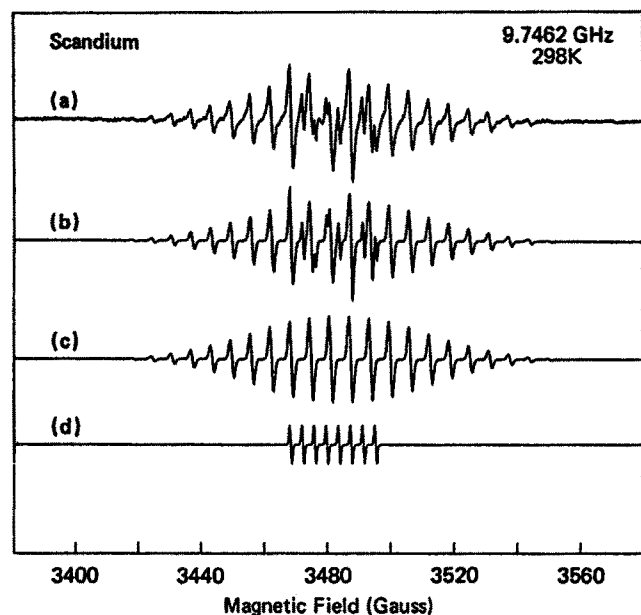


Figure 4. a) EPR spectrum of a room-temperature toluene solution containing scandium metallofullerenes; b) superposition of two simulated spectra arising from for an unpaired electron spin coupled to (c) three equivalent scandium nuclei and (d) a single scandium nucleus.

The superposition of Figs. 4c and 4d yields the simulation shown in Fig. 4b, in excellent agreement with experiment (Fig. 4a), suggesting that the EPR spectrum is due to 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. 4c) has a hyperfine coupling of 6.22 gauss. It is centered at  $g = 1.9985$ , close to the values found for  $\text{LaC}_{82}$ <sup>10</sup> (2.0010) and the  $\text{C}_{60}$  radical anion.<sup>26-29</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>30</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 proposed 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>30</sup>

The  $g$  value for  $\text{ScC}_{82}$  is 1.9998, also 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  $\text{LaC}_{82}$  (1.15 gauss).<sup>10</sup> The hyperfine coupling calculated for  $\text{Sc}^{+2}$  using unrestricted Hartree-Fock wave functions is -120 gauss, more than 30 times larger than the measured value. Thus  $\text{ScC}_{82}$  can also be characterized as having essentially a +3 oxidation state for the metal atom. 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  $\text{Sc}$  and  $\text{Sc}_3$  species in mass spectra) either have very broad EPR lines or are diamagnetic, with the scandium valence electrons paired either in the metal dimer orbitals or in orbitals of the fullerene cage. This is in sharp contrast with the results of Knight and co-workers, who detected an EPR spectrum for  $\text{Sc}_2$  in rare-gas matrices at 4.2K and concluded that  $\text{Sc}_2$  has a  $^5\Sigma$  ground state.<sup>31</sup> Similar results for metallofullerenes with 1, 2 and 3 scandium atoms have recently been reported by Shinohara et al.<sup>23</sup> The suggestion that the discandium metallofullerenes are diamagnetic can be checked directly using  $^{45}\text{Sc}$  NMR.<sup>32</sup> NMR experiments may be done on systems that are paramagnetic;<sup>33</sup> the  $^{45}\text{Sc}$  NMR resonances of the  $\text{ScC}_{82}$  and  $\text{Sc}_3\text{C}_{82}$  will be split by sizable hyperfine couplings

( $\sim 10^4$  ppm), and thus will appear well away from the chemical shift region of diamagnetic Sc-containing molecules or complexes ( $\sim 10^2$  ppm). A  $^{45}\text{Sc}$  NMR experiment on a  $\text{CS}_2$  solution of  $\text{CS}_2$ -extracted Sc metallofullerenes is shown in Figure 5. A somewhat asymmetric resonance is found at 35 ppm, and does *not* shift with temperature, confirming the diamagnetic nature of the dominant  $\text{Sc}_2\text{C}_{2n}$  species. The total sample mass was 10 mg, while comparison of the peak integral with a Sc standard gives a value of 90  $\mu\text{g}$  for the mass of the scandium metallofullerenes ( $\sim 1\%$ ). The apparent structure on the peak may result from differences in the chemical shift for cages with different numbers of carbons.

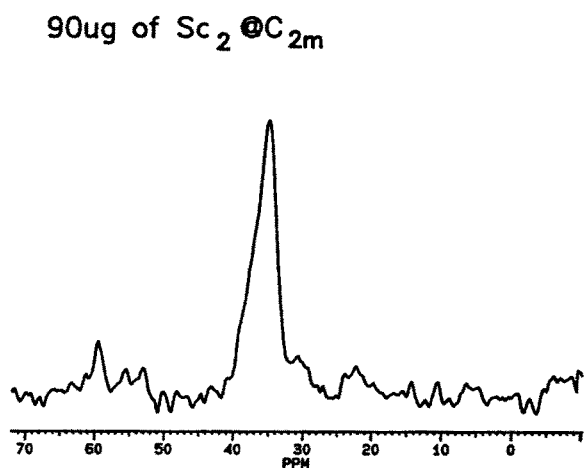


Figure 5. 121.5 MHz  $^{45}\text{Sc}$  NMR spectrum of a  $\text{CS}_2$  solution of  $\text{CS}_2$ -extracted Scandium metallofullerenes.  $4.1 \times 10^6$  scans were acquired.

The spectrum is broadened by quadrupolar coupling. It may be possible to learn about the mobility of the scandium atoms within the cage by relating the relaxation due to this coupling to the rotational dynamics of fullerenes in solution.<sup>32</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 and NMR spectroscopy. The number of metals which form metallofullerenes is growing.  $\text{UC}_{2n}$  species,

with  $2n \geq 28$ , and diuranium metallofullerenes with  $2n \geq 50$  have been reported,<sup>25</sup> and the first air and solution stable  $\text{C}_{60}$  metallofullerenes ( $\text{CaC}_{60}$ <sup>34</sup> and  $\text{FeC}_{60}$ <sup>35</sup>) have been found. Purification of metallofullerenes, which are still only available in small quantities, has been frustratingly slow and difficult. Nevertheless, we are very hopeful that it can be accomplished. The possibilities that these novel species offer, both for scientific study and for practical applications, are very exciting and still largely unexplored.

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