# General and Inorganic Chemistry

## Synthesis and identification of endohedral metallofullerenes La@$C_{82}$

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The effect of the procedure of preparation of lanthanum-graphite electrodes and the regime of their evaporation in the electric arc on the yield of endometallofullerene La@$C_{82}$ has been studied. La@$C_{82}$ was identified by ESR spectroscopy, optical spectroscopy, and mass spectrometry. The fractional extraction of the fullerene-containing soot with *o*-xylene makes it possible to separate La@$C_{82}$ from higher fullerenes containing no metal atoms and to obtain fullerene extracts enriched in La@$C_{82}$.

**Key words:** fullerenes, endohedral complexes, endometallofullerenes, La@$C_{82}$; ESR spectra.

Endometallofullerenes (M@$C_{2n}$) contain metal atoms inside fullerene molecules. The formation of such compounds is most typical of $C_{82}$ with the third group metals (Sc, Y, and the majority of lanthanides).[1] The unique structure and physical and chemical properties of endometallofullerenes are of great interest in the search for new molecular ferromagnets, metals, and superconductors. However, the properties of these compounds are as yet poorly studied due to their poor accessibility. The known procedures of the synthesis of M@$C_{2n}$ in the electric arc make it possible to obtain only microamounts of these compounds.[1,2] Therefore, improvement of the methods for the synthesis of M@$C_{2n}$ is one of the current problems in the area of chemistry and physics of carbon clusters. There are no published data on the effect of procedures for the preparation of metal-containing graphite electrodes and conditions of their evaporation in the electric arc on the yield of M@$C_{2n}$.[1,2,12] This work is devoted to the search for ways of optimization of the synthesis of endometallofullerenes by the electric-arc evaporation of metal-containing electrodes.

### Experimental

Graphite electrodes ("especially pure grade"-7-3 trade mark) containing lanthanum were used to obtain endometallofullerenes La@$C_{2n}$. A hole 2.9 mm in diameter was drilled from two ends in the center of the graphite rod (6×150 mm). Lanthanum metallic filings were mixed with graphite powder and graphite cement (GC trade mark, Dylon Industries Inc.) as a binder in a weight ratio of 1 : 0.57 : 1.43. The blend prepared was thoroughly stirred, packed in the hole of the graphite electrode, and carefully molded up to a final weight content of ~30% of the total weight of the electrode. The La/C ratio varied in different experiments from 0.5 to 1.5%. The electrode rods thus modified were thermally treated in three stages: 1) treatment in a vacuum furnace for 4—5 h at 130 °C; 2) heating for 4 h at 1100 °C; and 3) thermal treatment directly in the reactor *in vacuo* ($10^{-3}$ Torr) for 1 h at 1800 °C; the temperature was achieved by passing a direct current of 190—200 A through the electrodes.

Endometallofullerenes La@$C_{2n}$ were synthesized in an installation modified for this purpose, whose main structural features have been described previously.[3] The installation allows the variation of conditions of evaporation of rods in the

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electric arc in wide ranges, namely: to work with direct or alternating current, to vary the distance from the arc to the surface cooled with water, to vary the spatial arrangement of electrodes (horizontal or vertical arc), and to control the evaporation of the rod instrumentally and visually.

The method of two-step fractional extraction was used to extract endometallofullene-containing soot samples. At each stage of the extraction, a weighed soot sample (2—4 g) was placed in a flask with toluene or *o*-xylene (100 mL for the 1st stage or 150 mL for the 2nd stage). The solvents were preliminarily dried and distilled in an atmosphere of argon. Fullerenes were extracted from the soot for 3 h in an argon atmosphere at the boiling point of the solvent. Then the solution of fullerenes was thoroughly filtered off from the soot, and the solvent was distilled off on a rotary evaporator. The residue obtained was evacuated for 1 h at 90 °C and stored in a desiccator in an argon atmosphere.

Exclusion gel chromatography was used for the preliminary separation of light fullerenes and concentration of the fraction of endometallofullerenes. The fractions were separated on a Millikhrom chromatograph (column 4×200 mm, silanized silica gel Silasorb SPH 600 as the adsorbent); *o*-dichlorobenzene was used as the eluent, the rate of elution was 100 or 200 mL $min^{-1}$, and the spectrophotometric detection was performed at 360 nm.

Endometallofullerenes were identified by ESR spectroscopy, mass spectrometry, and spectrophotometry. ESR spectra were recorded on a Varian E-104A radiospectrometer (USA) in the X-range (≈9 GHz) at ~20 °C. Samples for ESR measurements were prepared as solutions in *o*-dichlorobenzene in standard quartz tubes with an inner diameter of 3 mm. The samples were thoroughly evacuated from oxygen by multiple freezing—thawing out, then the tubes were sealed *in vacuo*. The concentration of endometallofullerene was estimated by comparison of the intensity of its ESR signal with the signal of the standard solution of the nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl in *o*-dichlorobenzene.

The mass spectrometric analysis was performed on an MSBKh time-of-flight mass spectrometer (plant "Elektron," Sumy, Ukraine) with ionization by *Cf*-252 decay products at an accelerating voltage of 15 kV. Optical spectra of La@$C_{82}$ (toluene extract, concentration 2 mg $mL^{-1}$) were recorded in the near IR region (700—1100 nm) on an HP-8453 spectrophotometer (Hewlett-Packard).

## Results and Discussion

The incorporation of a metal into the electrode creates inhomogeneity in the graphite rod, which results in an unstable combustion of the arc and a decrease in the total yield of fullerenes to 1—4% as compared to pure graphite electrodes.

In addition, when compounded electrodes are evaporated, convection flows in the arc result in scattering of the blend as large particles, which decreases sharply the yield of fullerenes and suppresses completely the formation of endometallofullerenes. This difficulty was eliminated by the insertion of the graphite cement in the composition of the blend, which made it possible to obtain more uniform electrodes, whose central part evaporates in the arc in a stable regime. The three-step thermal treatment was used for the preparation of these electrodes. At the first stage of the thermal treatment (130 °C, 4—5 h), the graphite cement is solidified, after which the electrode rod can be heated to 3000 °C without destruction. The second stage of the thermal treatment (1100 °C, 4 h) is necessary to transform the organic binder, which comprises the graphite cement, to carbon. The most important is the final stage of the thermal treatment of the electrode rods directly in the installation (1800 °C, 1 h). This stage favors the formation of carbide $LaC_2$, the presence of its vapor in the arc being the necessary condition for the formation of La@$C_{2n}$. In addition, at a temperature of about 1800 °C, the electrodes are almost completely purified from oxygen and other gases adsorbed in pores of the rod.

It was of interest to reveal the dependence of the yield of endometallofullerenes on the distance between the arc and the cooled wall of the reactor, on which the soot is condensed, because we have previously observed that the yield of more high-molecular fullerenes ($C_{70}$ and higher) increases as this distance decreases.[4,12] When the La electrode is placed in the center of the reactor (the distance to the cooled wall is 90 mm), the $C_{70}/C_{60}$ ratio in the *o*-xylene extract (soot-1) is equal to 15 : 85. The yield of endometallofullerene (La@$C_{82}$) is very low (Table 1). It was detected by mass spectrometry (Fig. 1) only after exclusion chromatography of the *o*-xylene extract. When the arc approached the wall at a distance of 50 mm (the other parameters of the reactor were unchanged), an increase in the yield of both higher fullerenes ($C_{70}/C_{60}$ = 21 : 79) and endometallofullerenes (soot-2) was observed. The content of La@$C_{82}$ in the *o*-xylene extract, according to the ESR data, was equal to 0.14% (see Table 1). The mass spectrum of the extract exhibited an ion with $m/z$ 1123 corresponding to La@$C_{82}^+$, and the optical spectrum contained the characteristic absorption band of La@$C_{82}$ at 1000 nm (Fig. 2). It can be seen from Table 1 that the change in the helium pressure from 80 to 120 Torr (soot-3) resulted in a threefold increase in the yield of endometallofullerenes, while the yield of high fullerenes remained unchanged ($C_{70}/C_{60}$ = 21 : 79). The content of La@$C_{82}$ in the *o*-xylene extract of this sample of the soot was 0.42%.

The low stability of endometallofullerenes toward oxygen and peroxide radicals imposes additional demands on the choice and purity of organic solvents, which are conventionally used for extraction.[5,6] Carbon

**Table 1.** Effect of the helium pressure ($p$) and distance between the arc and the cooled wall of the reactor ($R$) on the yield and composition of the *o*-xylene extract of endometallofullerene soots obtained at d.c. of the arc of 90 A and voltage of the arc of 28 V

| Soot | $p$ /Torr | $R$ /mm | Content of fullerenes in soot (%) | $C_{70}$ : $C_{60}$ in extract | Content of La@$C_{82}$ in extract (%) |
|---|---|---|---|---|---|
| 1 | 80 | 90 | 4.2 | 15 : 85 | Traces |
| 2 | 80 | 50 | 1.1 | 21 : 79 | 0.14 |
| 3 | 120 | 50 | 1.7 | 21 : 79 | 0.42 |

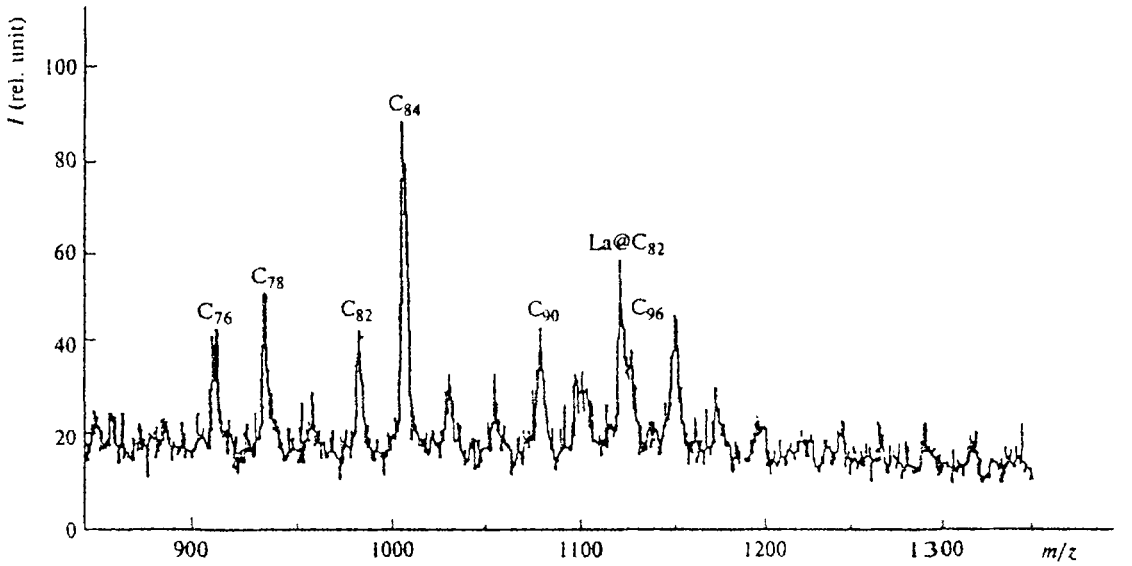


**Fig. 1.** Mass spectra (850 < $m/z$ < 1300) of the *o*-xylene extract of soot-1 after exclusion chromatography.

disulfide was excluded from this series due to its toxic character and explosion hazard, although it is known that it dissolves fullerenes and endometallofullerenes well.[7] In our experiments, endometallofullerenes were extracted in an inert atmosphere using toluene or *o*-xylene freshly distilled in an argon atmosphere. *o*-Xylene turned out to be an efficient solvent for the extraction of La@$C_{82}$ from the endometallofullerene soots.

A small volume of the solvent (100—150 mL) and the two-step extraction scheme were used to obtain endometallofullerene extracts: I, *o*-xylene (100 mL); II, *o*-xylene (150 mL). It can be seen from the data presented in Table 2 that soot-2 and soot-3 are characterized by the same ratio of $C_{70}$ and $C_{60}$ both in the first and second *o*-xylene extracts. However, these extracts differ substantially by the content of endometallofullerene. For soot-2, the amount of La@$C_{82}$ in extract II is by 42% greater than that in extract I.

Thus, this simple extraction scheme makes it possible to obtain *o*-xylene extracts enriched in endometallofullerenes.

The mass spectrum of the first *o*-xylene extract of soot-3 exhibits an ion with $m/z$ 1123 corresponding to the molecular ion of La@$C_{82}$ along with molecular ions of higher fullerenes $C_{78}$ ($m/z$ 936), $C_{82}$ ($m/z$ 984), and $C_{84}$ ($m/z$ 1008).

In the mass spectrum of the second *o*-xylene extract in the region of 850 < $m/z$ < 1300, an ion with $m/z$ 1123 (La@$C_{82}$) predominates (Fig. 3). Therefore, the two-step extraction scheme suggested makes it possible to separate efficiently the lanthanum-containing fullerene from higher fullerenes, which does not contain encapsulated metal atoms.

Thus, taking into account the differences in the physicochemical properties of fullerenes and endometallofullerenes (by the solubility in *o*-xylene and the character of the interaction with the soot), *o*-xylene

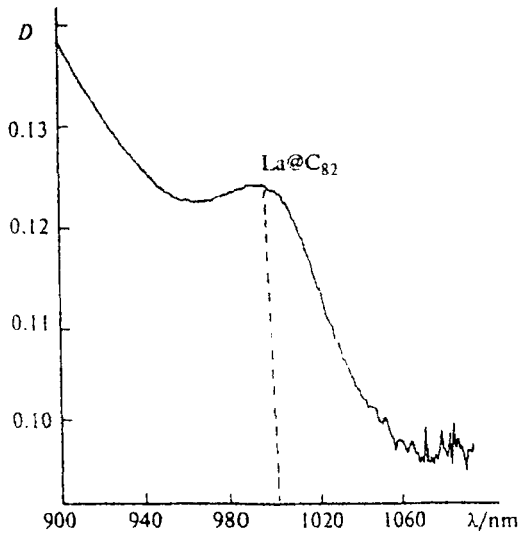


**Fig. 2.** Absorption spectrum in the near IR region of *o*-xylene extract II of soot-2 in toluene (2 mg $mL^{-1}$).

**Table 2.** Composition of *o*-xylene extracts obtained by the two-step extraction method according to the scheme: *o*-xylene (100 mL) (I)—*o*-xylene (150 mL) (II)

| Soot | Extract | $C_{70}$ : $C_{60}$ | Content of La@$C_{82}$ (%) |
|---|---|---|---|
| 2 | I | 21 : 79 | 0.12 |
| | II | 21 : 79 | 0.17 |
| 3 | I | 21 : 79 | 0.36 |
| | II | 21 : 79 | 0.46 |

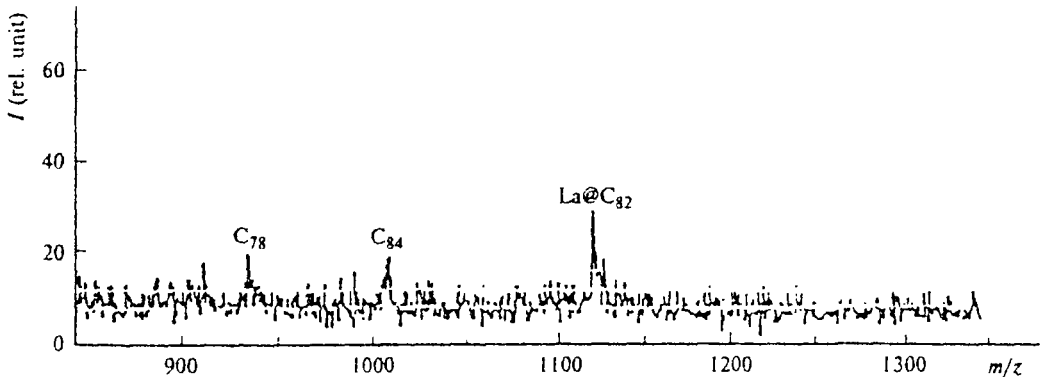


**Fig. 3.** Mass spectrum (850 < $m/z$ < 1300) of *o*-xylene II extract of soot-3.

extracts with a low content of higher fullerenes, but enriched in $La@C_{82}$ by 30—40%, can be obtained already at the stage of the extraction.

The ESR spectrum of the second *o*-xylene extract of soot-3 exhibits the hyperfine structure (HFS) from eight narrow lines of approximately equal intensities, the half-width of the lines (the distance between points of the maximum slope) is $\Delta H$ = 0.14±0.01 G, the distance between the HFS lines is 1.15±0.01 G, and the *g*-factor is 2.0011±0.0001 (the position of the fourth component in the magnetic field) (Fig. 4). The similar spectra were also observed in the other extracts. This spectrum corresponds by its parameters to the ESR spectra of lanthanum-containing fullerenes of the $La@C_{82}$ type.[8,10,12]

The HFS is caused by the interaction of a lone electron with the spin moment of the lanthanum nucleus ($I$ = 7/2). The small value of the HFS constant (1.15 G instead of 186 G, which is characteristic of pure $^{139}La$) testifies that less than 1% of the spin density of an unpaired electron is localized on the lanthanum nucleus, and most of it is delocalized on the carbon shell of the complex.[8]

In addition to the main octet, the ESR spectrum distinctly exhibits the HFS components of one more octet signal with approximately the same value of the half-width of the lines (0.15±0.01 G), the distance between the HFS lines of 0.82±0.02 G, and $g$ = 2.0003±0.0001 (see Fig. 4). It is also evident that the fourth, seventh, and eighth HFS components of the second octet partially overlap the fifth, seventh, and eighth components, respectively, of the first octet. Both octet ESR signals are completely identical to the signals of two different isomers of $La@C_{82}$, which have been described previously. Along with the lines of two main octets, weak HFS lines on nuclei of the $^{13}C$ isotope and HFS lines caused likely by the presence of insignificant amounts of $La@C_{76}$ isomers also make a contribution to the total intensity of the ESR spectra of the extracts.[8,10,12]

The total intensity of the ESR signals of $La@C_{82}$ in the extracts was equal to 0.05—0.08 mmol $L^{-1}$. The intensity of the second octet is 3—4 times lower than that of the first octet, and the signals of the other isomers are still weaker by 1—2 orders of magnitude.

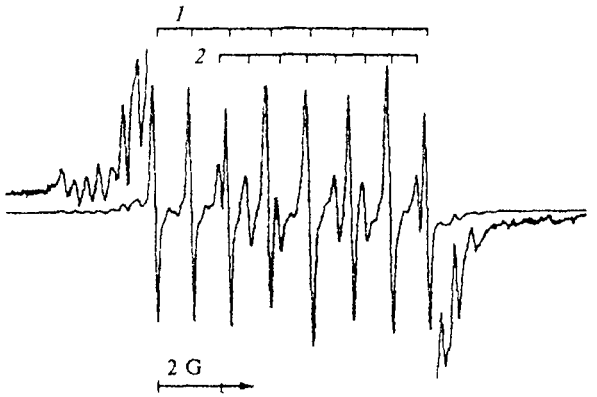


**Fig. 4.** ESR spectrum of the *o*-xylene extract II of soot-3 in *o*-dichlorobenzene (25 mg $mL^{-1}$) in the absence of oxygen. The components of the 1st octet (*1*) and 2nd octet (*2*) are indicated. Conditions of detection: room temperature, microwave power $P$ = 1 mW, frequency of the magnetic field modulation 100 kHz, amplitude of the modulation $H_m$ = 0.025 G, rate and time constant of sweeping the magnetic field 1.25 G $min^{-1}$ and 0.25 s, amplification $2.0\times10^2\times10$ (detection of the main signal) and $2\times10^3\times10$ (detection of the "wings" of the signal).

Thus, the conditions under which endometallofullerenes form differ substantially from those of the formation of normal fullerenes ($C_{60}$, $C_{70}$, *etc.*). The methods for the preparation of compounded rods and the regimes of their evaporation exert a great effect on the yield of metallofullerenes. An increase in the pressure of helium and approach of the electrodes to the cooled surface are accompanied by an increase in the yield of $La@C_{82}$. Two-step extraction with *o*-xylene results in an enrichment of the second extract in $La@C_{82}$ and a decrease in the fraction of higher fullerenes in this extract.

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