Endohedral Metallofullerenes: A Convenient Gram-Scale Preparation

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We have examined various parameters of the electric arc synthesis of endohedral metallofullerenes (EMFs or M@C$_{2n}$). The influence of some experimental parameters (M/C ratio, helium vapor pressure, and values of the direct current arc) on yields of EMFs has been studied. The optimization of these parameters allows us to bring the EMF yield to a record level of 6−8% of the primary soot mass. Furthermore, a selective extraction sequence [*o*-xylene (five cycles) − dimethylformamide (seven cycles)] has been studied in detail in order to apply this technique to the estimation of the EMF yield. It has also been shown that polar organic solvents, among them dimethylformamide (DMF), dimethylacetamide (DMA), and dimethylsulfoxide (DMSO), are the most favorable ones for a selective extraction of EMF.

Introduction

The paramagnetic endohedral metallofullerenes (EMFs or M@C$_{2n}$) hold much promise as new materials with unique magnetic, electrical, and optical properties.[1−5] Therefore, they are very attractive for various technical applications. Namely, it was suggested that La@C$_{82}$ might be used for measurement of the oxygen content in microheterogeneous systems as well as an effective contrast agent for NMR imaging.[4,6] EMFs are usually prepared by arc-burning of metal/graphite composite rods.[3] At present, this method permits chemists to obtain the soot containing no more than 1.5% of EMFs.[3,7,8] It must be emphasized that the isolation of EMFs from the soot is a very time-consuming procedure.[7−11] These two factors make EMFs difficult to produce and allow isolating these carbon clusters only on a milligram scale.[3,7,8] Therefore, the development of advanced methods for the synthesis and isolation of EMFs is very important. Difficulties associated with the EMF isolation[9−11] hinder an estimation of the efficiency of their formation, hence making impractical an optimization of electric arc parameters for the EMF-rich soot production. To solve this problem, we have suggested to use a simple selective extraction sequence[12] that has been recently developed. Applying this technique for the estimation of the EMF yields requires an in-depth study of this method to make sure that it permits a total removal of EMFs from the soot.

Here we report the new details of the two-step selective extraction scheme which allow using this procedure for the control of M@C$_{2n}$ (M = La or Y) syntheses. We also show how some experimental parameters of the arc burning of metal/graphite composite rods in a helium environment affect the EMF formation. The characteristic data of both La@C$_{2n}$ and Y@C$_{2n}$ isolated on a gram scale (mass spectra, X-ray fluorescence analysis, and EPR spectra) are presented and discussed as well.

Experimental Section

Samples of the EMF containing soot were synthesized in an electric arc reactor (see Figure 1). The reactor was equipped with graphite composite electrodes containing lanthanum or yttrium. Anodes were Ø 6 × 160 mm spectral pure graphite rods in which a Ø 3 × 160 mm hole was drilled and filled with a mixture of a graphite cement, metal, and graphite powder (Table 1). Cathodes, 12−16 mm in diameter, were made of

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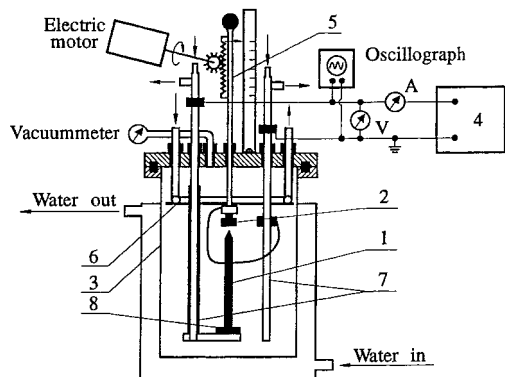
Figure 1. Scheme of the apparatus for the EMF synthesis: 1, composite graphite electrode to be volatilized; 2, nonvolatilized graphite electrode (cathode); 3, stainless steel cavity cooled by water from outside; 4, direct current arc source; 5, stainless steel rod; 6, water-cooled copper screen; 7, inlets cooled by water; 8, graphite ring.

Table 1. Content of the Metal in a Composed Electrode Used for the EMF Synthesis and the Yield of M@C$_{2n}$

metal	atomic ratio of metal to carbon, %	yield of M@C$_{2n}$, %
La	0.5	2.4
	1.0	6.0
	1.5	2.6
Y	0.5	2.5
	1.0	8.0
	1.5	2.9

Table 2. Values of Helium Vapor Pressure (P_{He}), Values of the Direct Current Arc (I_{arc}), and the Yield of M@C$_{2n}$

P_{He}, Torr	I_{arc},[a] A	yield of La@C$_{2n}$	yield of Y@C$_{2n}$, %
70	90	2.5	3.5
90	90	2.3	2.6
120	90	6.0	8.0
120	110	2.3	2.9
120	70	2.0	3.0

[a] The value of the voltage arc = 26–28 V, the arc length = 5 mm; the distance between the electric arc and a cooling surface of the reactor is equal to 50 mm.
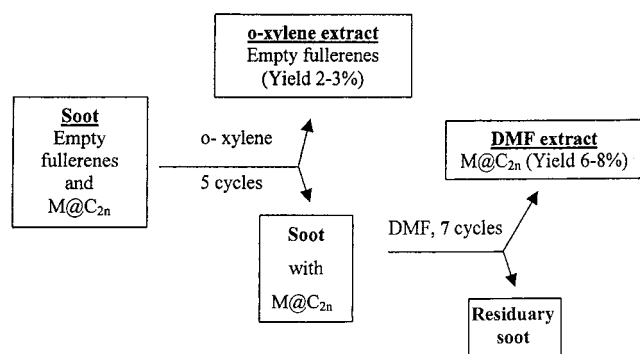

Figure 2. Scheme of selective extraction sequence used for the EMF isolation.

MPG-8 graphite. The electric arc parameters used are listed in Table 2.

EMFs were extracted from the EMF-containing soot by the organic solvents under argon following the sequence shown in Figure 2. In the first stage, the soot was treated with *o*-xylene, its molecules having a low electric dipole moment ($P = 0.62$ D). The weighed sample of soot ($\approx$10 g) was placed in a filter-paper vessel which, in turn, was placed into a glass flask containing 500 mL of *o*-xylene, and the extraction procedure was performed for 3 h at the boiling point of the solvent under argon. The resultant solution was thoroughly filtered off, the solvent was evaporated on a rotary evaporator, and the extract was dried for 1 h at 90 °C in a vacuum. The cycle was repeated five times, the fifth portion of *o*-xylene emerging virtually colorless. This colorless fraction served as a performance criterion in deciding when to end the *o*-xylene extraction stage (see scheme in Figure 2).

After the *o*-xylene treatment, the soot was subjected to the second extraction with such polar solvents as DMF, DMA, or DMSO. Again, the soot sample in a paper-made vessel was placed in a flask containing 500 mL of the solvent, and the extraction procedure was performed for 3 h at the solvent boiling point under argon. The obtained solution was filtered off, the solvent was evaporated, and the residue was dried for 1 h at 90 °C in a vacuum and weighed. Note the last procedure, removing most of the solvent, is enough in order to produce the extracts fixed by both their weight and their composition. The cycle with the polar solvent was repeated six times.

Mass spectroscopic analysis was performed by the laser desorption/ionization (LDI-TOF) technique, using a time-of-flight mass spectrometer (Finnigan: Vision 2000). Radiation pulses of 3 ns from N$_2$ laser operating at 337 nm were used to desorb the species from coated stainless steel plate, and the negative ions formed were detected in linear mode. In addition, the MSBKh mass spectrometer using ionization with ^{252}Cf decay products was applied.

The elemental analysis was performed using X-ray fluorescent spectroscopy on a VRA-30 analyzer.

EPR spectra were measured on a Varian E-104A radiospectrometer in the X range (9 GHz) at room temperature under the conditions precluding the distortion of the line shape. The samples for EPR measurements were prepared as solutions in standard quartz tubes with an inner diameter of 3 mm. The samples were thoroughly deoxygenated by multiple freeze–thaw cycles before the tubes were sealed in vacuum.

Results and Discussion

The usual way to obtain EMFs is a three-stage procedure: (1) synthesis of the soot containing EMFs along with empty fullerenes by the arc technique, (2) concurrent extraction of both EMFs and empty fullerenes, and (3) isolation of EMFs from an extract by a laborious HPLC method.

First of all, to obtain the EMF-rich soot, it is crucial to elucidate a dependence of the EMF yield on electric arc parameters and on an apparatus design. To this end, we have to control the M@C$_{2n}$ formation correctly. By applying the selective extraction sequence (see Introduction), we were able to estimate the M@C$_{2n}$ formation realistically. As shown earlier,[12] this two-step extraction procedure with *o*-xylene as the first solvent and dimethylformamide (DMF) as the second solvent makes it possible to isolate a mixture of EMFs avoiding the use of a laborious HPLC technique. We have successfully developed this extraction method to provide the complete EMF isolation (see below).

Endometallofullerenes La@C$_{2n}$ and Y@C$_{2n}$ were prepared by the dc arc discharge method in a homemade reactor equipped with graphite composite electrodes containing lanthanum or yttrium. It is safe to assume that it should be an average optimum content of the metal to achieve the highest yield of EMFs. To establish the relationship between the EMF yield and the composition of graphite electrodes, we used electrodes containing different amounts of lanthanum or yttrium. The electrodes were prepared according to a three-stage process described previously.[5] In the different experiments the ratio of La/C or Y/C varied from 0.5% to 1.5% (see Table 1). From data presented in Table 1, it is clear

Table 3. Yield and the Composition of the DMF Extract in the DMF Cycle of the Extraction Scheme Employed

sample of the M@C_{2n} containing soot		yield of the DMF extract at the cycle			intensity of molecular masses in the mass spectrum of the DMF cycle fraction[a]					
M	wt, g	no. of the cycle	mg	%	M@C_{82}^-	M@C_{80}^-	M@C_{2n}^-	C_{60}^-	C_{70}^-	C_{2n}^-
La	9.975	1	146	24	s	m	w	vw		
		2	154	25	s	m	w			
		3	140	23	s	m	w			
		4	85	14	s	m	w			
		5	62	10	s	m	w			
		6	12	2	s	m	w			
		7	11	2	s	m	w			
		total yield	610	100						
Y	9.893	1	200	25	s	m	w	vw		
		2	190	24	s	m	w			
		3	176	22	s	m	w			
		4	120	15	s	m	w			
		5	70	9	s	m	w			
		6	18	2	s	m	w			
		7	16	2	s	m	w			
		total yield	790	100						

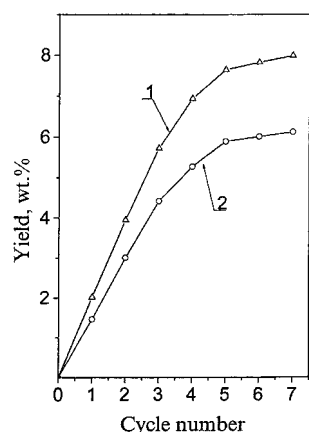[a] s = strong, m = medium, w = weak, vw = very weak.

Figure 3. Dependence of the yield of the M@C_{2n} fraction on the number of the DMF extraction cycle: M = Y (curve 1) and M = La (curve 2).

that the M/C ratio ≈1.0% is the best ratio for both the metals. The use of such electrodes may increase the yield of M@C_{2n} by a factor of 2.5 or even more.

The experimental data summarized in Table 2 show that the yield of EMFs is a subject to wide variations depending on helium vapor pressure and a value of direct current. Hence, these parameters have a significant effect on the EMF formation. The use of optimal values of these parameters may bring the yield of M@C_{2n} to the level of 6−8% of the primary soot. This provides a real possibility to produce grams of EMFs. For example, one can obtain 0.8 g of Y@C_{2n} from 10 g of Y@C_{2n}-containing soot. Presently, both the Y@C_{2n} and La@C_{2n} yields are on a record scale and exceed the reported EMF yields[3,8] by a factor of 5−7.

Below we will focus on the M@C_{2n} isolation that is a determining factor in the estimation of the EMF formation. To achieve the best result on the M@C_{2n} isolation, we have added six auxiliary DMF cycles to the second step of the previously developed extraction sequence[12] (see scheme in Figure 2). Table 3 and Figure 3 demonstrate how the yield of EMFs depends on the number of the extraction cycles. The addition of the six DMF extraction cycles increases the isolated amount of EMFs by a factor of 4. We have found the maximum amount of EMFs (90 wt %) to release from a soot sample during

the five DMF cycles. Thus, the extraction of EMFs with the five or six DMF cycles is sufficient to estimate the M@C_{2n} yield correctly.

The next problem to investigate is whether it is possible to improve the EMF separation by raising extraction temperature. To answer this question, we tested DMF, DMA, and DMSO which have different boiling temperatures. The molecules of all the chosen solvents have similar electric dipole moments which are close to that of La@C_{82}[13,14] ($P = 3.8$ D). On the basis of data presented in Table 4, one can see that the EMF isolation hardly depends on temperature in the range of 150−190 °C. Consequently, all the polar solvents selected may be equally used to extract EMFs.

Table 4 also includes the data on the composition of the extracts obtained by the two-step sequence. These data indicate that the *o*-xylene extracts mainly mixtures of empty fullerenes contain a very small amount of M@C_{2n}, while the polar solvent extracts mixtures of EMFs contain little or no empty fullerenes. For example, the results of the X-ray fluorescence analysis show the contents of La or Y in the polar solvent extracts to be 11.8−12.3 or 7.9−8.1 wt %, respectively. One can see that the metal content almost coincides with the theoretical lanthanum content in La@C_{82} (12.4 wt %) and yttrium content in Y@C_{82} (8.3 wt %). On the basis of elemental analysis data, all the EMF samples dried up to the weight fixed contain about 2−3 wt % of N (see Table 4). Therefore, similar to empty fullerenes, these EMF samples hold a fixed amount of the solvent that is bonded to EMF clusters. But the latter does not restrict applying our extraction sequence to the control of the EMF formation since it allows us to isolate reproducibly EMFs as powders which are characterized by a fixed composition (see experimental part and Table 4). To remove the co-crystallized solvent, these extracts have to be heated for a long time at temperatures higher than 90° C. The production of solvent-free EMFs is being developed.

All the extracts of M@C_{2n}-containing soot have been characterized by mass spectrometry and EPR. The most intense peaks in the mass spectra of the *o*-xylene extracts correspond to the molecular masses of C_{60}^- (M/z = 720) and C_{70}^- (M/z = 840) while the weakest peaks

Table 4. Yield and the Composition of Different Extracts Obtained from the M@C$_{2n}$ Containing Soot According to the Extraction Scheme

| | | | yield (%) of the extract obtained from the M@C$_{2n}$ containing soot | | extract composition | | | | |
| | | | | | content of fullerenes,[a] % | | | content of nitrogen (N) and metal (M)[b] | |
solvent	P, D	bp, °C	M	%	C$_{60}$	C$_{70}$+C$_{2n}$	M@C$_{2n}$ solvated	N (wt %)	M (wt %)
o-xylene	0.62	143	La	2.5	80	≈20	>0.1		
			Y	2−3	80	≈20	>0.1		
DMF	3.86	152	La	3−6			≈100	2.23	12.3 ± 0.2
			Y	4−8			≈100	2.38	8.1 ± 0.2
DMA	3.81	165	La	3−5			≈100	3.08	12.1 ± 0.2
DMSO	3.96	189	La	4−5			≈100		11.8 ± 0.2
			Y	3−5			≈100		7.9 ± 0.2

[a] The content of empty fullerenes was determined by the optical spectrometric method; the presence of M@C$_{2n}$ in o-xylene extracts was tested by the EPR method. [b] The content of nitrogen was determined by a traditional elemental analysis; the amount of metal was found by the X-ray fluorescence analysis.
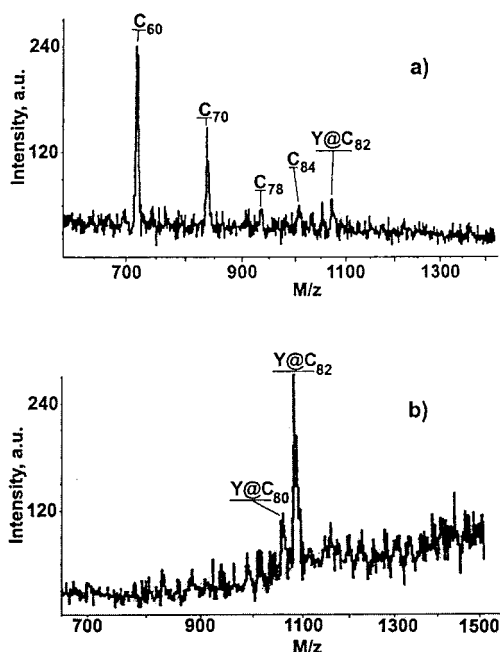

Figure 4. Mass spectra of two extracts from the soot sample containing Y@C$_{2n}$: o-xylene extract (a) and DMF extract (b); ionization by ^{252}Cf decay products.

Figure 5. Mass spectra of the DMF extract from the La@C$_{2n}$ containing soot: ionization by ^{252}Cf decay products (a); laser desorption ionization (b).

correspond to the molecular masses of the highest fullerenes and M@C$_{82}$. For example, the mass spectrum of the o-xylene extract of the Y@C$_{2n}$-containing soot is presented in Figure 4a. The mass spectra of the o-xylene extracts are evidence that the empty fullerenes are preferably selected during the first stage of the extraction procedure.

The mass spectra of the DMF extracts containing Y@C$_{2n}$ and La@C$_{2n}$ are shown in Figures 4b and 5. All the mass spectra of DMF extracts exhibit molecular masses, which correspond to the molecular ions of M@C$_{2n}^{-}$. It should be noted that the mass spectra produced via ionization by ^{252}Cf decay products contain a poorer collection of the M@C$_{2n}$ molecular masses compared to that of LDI TOF mass spectra (Figures 4b and 5). For example, the LDI TOF mass spectrum of the DMF extract of the La@C$_{2n}$-containing soot exhibits a great variety of peaks in the range of molecular masses from 1099 to 1243, which corresponds to the molecular ions from La@C$_{80}^{-}$ to La@C$_{92}^{-}$ (Figure 5b). Whatever type of ionization, the mass spectra of DMF, DMA, and DMSO extracts have no peaks corresponding to molecular masses of empty fullerenes (C$_{60}$, C$_{70}$, and
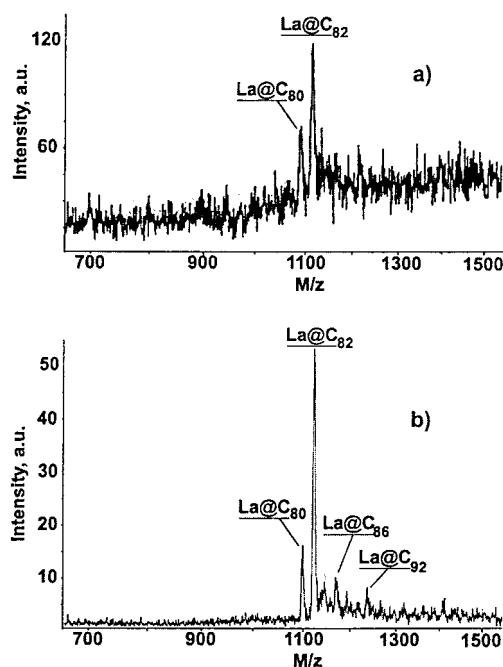
the higher ones); the most intense peak always corresponds to M@C$_{82}$ (see Table 3). The absence of empty fullerenes in the second stage extracts was earlier confirmed by HPLC and optical spectra.[12]

Electron paramagnetic resonance spectroscopy has been applied as a principal method for the identification of paramagnetic EMFs.[3,4] Figure 6 shows the EPR spectra of the DMF extracts in o-dichlorobenzene for two different soot samples containing La@C$_{2n}$ and Y@C$_{2n}$. Both the spectra presented are identical to the reported spectra in chlorobenzene, toluene, o-xylene, or CS$_2$.[3,15,16] It is noteworthy that, along with the major signals of La@C$_{82}$ or Y@C$_{82}$, some weak EPR lines are also observed in the spectra. These weak lines obviously arise from minor amounts of other La@C$_{2n}$ or Y@C$_{2n}$.

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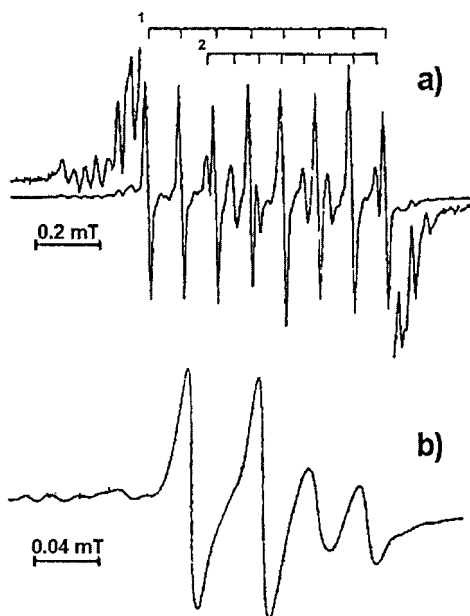
Figure 6. EPR spectra of DMF extracts obtained from the $M@C_{2n}$-containing soot in *o*-dichlorobenzene: M = La (a) and M = Y (b).

Thus, the EPR spectra together with mass spectrometry and X-ray fluorescence analysis confirm that the polar solvent extracts are the mixtures of EMFs, in which $M@C_{82}$ is the main component.

Summary

This study has shown that there is a real possibility to prepare gram amount of a mixture of EMFs avoiding the HPLC technique. For the first time the relationship between some experimental parameters of the arc burning of metal/graphite composite rods in a helium environment and the EMF formation was revealed. The experimental parameters that allow producing the soot with a record-scale content of EMFs were indicated. We were the first to described in detail the selective extraction sequence that permitted its successful use for the estimation of the EMF formation. In accordance with X-ray fluorescence analysis, mass spectrometry data, and EPR spectra, the isolated EMFs are defined as a mixture of various $M@C_{2n}$ containing $M@C_{82}$ as the main component. These samples of EMF also contain a certain amount of the co-crystallized polar solvent.