Synthesis of endohedral di- and monometallofullerenes $Y_2@C_{84}$, $Ce_2@C_{78}$, and $M@C_{82}$ (M = Y, Ce)

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Endohedral metallofullerenes $Y_2@C_{84}$, $Ce_2@C_{78}$, and $M@C_{82}$ (M = Y, Ce) were synthesized by the electric arc method and isolated from the soot using extraction with *o*-dichlorobenzene. Pure (98%) endohedral dimetallofullerenes $Y_2@C_{84}$ and $Ce_2@C_{78}$ were isolated for the first time from *o*-dichlorobenzene extracts using HPLC and characterized by mass spectrometry and spectrophotometry.

Key words: endohedral metallofullerenes, electric arc synthesis, extraction, high-performance liquid chromatography, mass spectrometry, spectrophotometry.

Unique structure of endohedral metallofullerenes (EMF) and diversity of their properties, depending on the nature of encapsulated metal and fullerene, excite great interest from the viewpoint of studying their chemical and physicochemical properties. It can be expected that success in the area of synthesis and investigation of the physicochemical properties of EMF would form a basis for practical use and creation of novel materials with unique electrical, magnetic, optical, chemical, and biological properties, for instance, organic ferromagnetics, laser and Seignette-electric materials, and pharmaceutical and radiopharmaceutical preparations.^{1–4}

However, EMF are poorly studied up to present. Published data on their chemical properties are virtually lacking. The main reason for this situation is restricted accessibility of EMF because of problems in their synthesis and isolation in preparative amounts.

The known methods for the synthesis of EMF (laser and electric arc vaporization of composite graphite electrodes) and traditional methods of their isolation from soot (extraction with toluene, carbon disulfide, *o*-dichlorobenzene (DCB)) make it possible to obtain extracts in low yield (0.5-3%) and EMF content (0.1-1%).^{1,5,6} Multistep HPLC is used to isolate pure EMF from the extracts. However, the chromatographic process is very labor-consuming because of the low EMF content in the extracts. Pure EMF (96–99%) have been prepared so far only in milligram quantities and are almost inaccessible for a wide range of researchers.¹

It should be mentioned that imperfect methods for EMF isolation prevent the optimization of conditions for their synthesis. As a rule, only final results are presented in the literature, while no conditions for the preparation of rare-earth metal-containing graphite electrodes are discussed and no analysis of the influence of the electric arc parameters and constructive features of electric arc setups on an increase in the yield of EMF in the soot is given. In this work, we synthesized for the first time and characterized endohedral dimetallofullerenes $Y_2@C_{84}$ and $Ce_2@C_{78}$ by the optimization of all steps of the EMF synthesis.

Experimental

The process of synthesis of EMF with yttrium and cerium includes four steps, each of which plays a substantial role in the synthesis: (1) preparation of the composite graphite electrodes containing rare-earth metals Y and Ce; (2) electric arc vaporization of the composite graphite electrodes and preparation of the EMF-containing soot; (3) isolation of fullerenes and EMF from the soot by extraction; (4) isolation of individual EMF by two-step HPLC.

The composite graphite electrodes containing rare-earth metals (yttrium or cerium) with the optimum ratio $M/C \sim 1\%$ were prepared as follows: (1) holes 2.9 mm in diameter were drilled at two sides in the center of a graphite rod (extra pure graphite for spectral analysis, O.S.Ch.-7-3 trade mark, 6×160 mm); (2) a blend was prepared: metallic yttrium (or cerium) filings were mixed with the graphite powder and graphite GC cement (Dylon Industries Inc.), which is used as a binding, in weighed ratios of 1: 0.57: 1.43 and 1: 0.56: 1.11 for Y and Ce, respectively; the prepared blend was thoroughly stirred, packed in the hole of the graphite rod, and carefully molded; (3) the rods were subjected to thermal treatment in three steps. Treatment in a vacuum oven (~ 10^{-3} Torr) for 4–5 h at 130 °C was carried out in the first step. At this temperature the graphite cement solidified. Then the rod can be heated to high temperatures (up to 3000 °C), not be afraid of its decomposition. In the second step, the thermal treatment continued for 4 h at 1100 °C

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in vacuo (~10³ Torr). This step is necessary to transform the binding, which is present in the composition of the graphite cement, into carbon. In the third step, the thermal treatment was carried out directly in an electric arc reactor for 30 min at 1800–1900 °C *in vacuo* (10⁻³ Torr). The necessary temperature was achieved by passing a constant electrical current (180–200 A) through the electrode. The latter thermal treatment resulted in the formation of metal carbides MC₂ (M = Y, Ce) in the composite electrode. Their presence in the arc as vapor along with carbon particles C₂ is a necessary condition for EMF formation.⁷ In addition, at ~1800 °C the electrodes are almost completely cleaned from oxygen and other gases adsorbed in pores of the rod, favoring more stable burning of the arc and increasing the EMF content in the synthesized soot.

The soot containing EMF with yttrium or cerium was prepared by the vaporization of the composite graphite electrodes in the electric arc reactor designed and produced by us.^{8–10} The optimum conditions for electrode vaporization in the arc are the following: helium pressure 120 Torr, arc current 80-90 A, voltage 27–28 V, arc length 5 mm, distance from the arc to the cooled reactor surface 50 mm, and rate of electrode vaporization 4 mm min⁻¹.

Endohedral metallofullerenes with yttrium and cerium were isolated from the soot by extraction with *o*-dichlorobenzene. A weighed sample of the soot (10–15 g) was loaded in a cellulose (Whatman Int. Ltd.) extraction thimbler, and the thimbler was placed in a glass flask containing 1 L of DCB (\geq 99% (GC), Sigma-Aldrich). Extraction was carried out in an argon atmosphere for 3–4 h at the boiling point of DCB (180.5 °C). Then a solution of fullerenes and EMF was thoroughly filtered (0.5 μ PTFE, Phenomenex Filter Membranes), the solvent was distilled off on a rotary evaporator, and the precipitate was dried for ~1 h. The extraction (usually seven—nine cycles) was carried out until a fresh portion of the solvent virtually stopped staining. The yield of the DCB extracts was ~5% of the soot weight.

To isolate individual EMF, multistep HPLC was used (HP-1050, Hewlett Packard Co.) with successive columns packed with sorbents of two types: Cosmosil Buckyprep ($20 \text{ mm} \times 250 \text{ mm}$) and Riges Buckyclutcher ($21 \text{ mm} \times 250 \text{ mm}$).

Mass spectrometric investigation was carried out on a timeof-flight mass spectrometer with laser desorption/ionization (MALDI-TOF, Voyager-DETM PRO BiospectrometryTM Workstation, Applied Biosystems, USA). A pulse nitrogen laser with the wavelength 337 nm, frequency 3 Hz, and pulse duration 0.5 ns was used. Positive and negative ions were detected in the reflectron mode. A sulfur (S₈) solution in toluene was used as the matrix. The sample under study and the matrix (in the molar ratio ~1 : 1000) were mixed and deposited as a microdrop on a metallic target, and the solvent was evaporated at room temperature to obtain a film of the substance under study.

Absorption spectra of the EMF samples in toluene were recorded in the wavelength interval from 300 to 1100 nm on a Varian Cary 500 Scan UV-Vis-NIR-spectrophotometer instrument in standard quartz cells 10 mm thick.

Results and Discussion

Along with empty fullerenes C_{60} and C_{70} and higher fullerenes (C_{76} , C_{78} , C_{82} , C_{84} , and others), DCB also

extracts EMF M@C₈₂ (M = Y, Ce) from the soot, which is confirmed by the data of mass spectrometry and HPLC. The yield of the DCB extracts reaches 5% of the soot weight, which is 2–3 times higher than the values known from literature.^{1,11} This result was obtained by the optimization of conditions for preparation of the composite graphite rods and their vaporization in the electric arc. The mass spectra and chromatograms of the DCB extracts containing EMF with yttrium and cerium are presented in Figs 1 and 2, respectively. It was found on the basis of the mass spectrometric and HPLC data that the content of EMF Ce@C₈₂ and Y@C₈₂ in the DCB extracts was 1–2% of the extract weight.

The obtained samples of the extracts of EMF with yttrium and cerium were used to isolate individual EMF $M@C_{82}$, $Y_2@C_{84}$, and $Ce_2@C_{78}$ by two-step HPLC. In the first step of HPLC, the DCB extract dissolved in *o*-xylene and containing EMF with yttrium or cerium was separated on the Cosmosil Buckyprep column using toluene as the eluent. In this step (see Figs 1, *b* and 2, *b*), fraction **A** or **B** containing, according to the mass spectrometric data, monometallofullerenes $M@C_{82}$, dimetallo-



Fig. 1. MALDI-TOF mass spectrum of positive ions (*a*) and the HPLC chromatogram (Cosmosil Buckyprep column, elution rate 18 mL min⁻¹, toluene as eluent) of the DCB extract of the soot containing EMF with yttrium (*b*). Here and in Figs 2–6 t_r is the retention time.



Fig. 2. MALDI-TOF mass spectrum of negative ions (*a*) and the HPLC chromatogram (Cosmosil Buckyprep column, elution rate 18 mL min⁻¹, toluene as eluent) of the DCB extract of the soot containing EMF with cerium (*b*).

fullerenes $M_2@C_n$ (M = Y, n = 84; M = Ce, n = 78), and fullerene C_{88} was separated from fullerenes C_{60} and C_{70} and higher fullerenes ($C_{76}-C_{110}$). In the second step, the collected fractions **A** and **B** were separated on the Regis Buckyclutcher column (toluene as eluent) (Figs 3, aand 4, a). As a result, compounds $M@C_{82}$ (Figs 3, cand 4, c) and $M_2@C_n$ (Figs 3, b and 4, b) were isolated. The separation process at the second step was repeated 2–3 times to obtain the high-purity (~98%) EMF samples.

The purity of the isolated endohedral monometallofullerenes $M@C_{82}$ (M = Y, Ce) and dimetallofullerenes $M_2@C_n$ was estimated using MALDI-TOF mass spectroscopy and HPLC analysis. The mass spectrum of positive ions and the chromatogram of pure EMF Ce@C₈₂ are presented in Fig. 5. The mass spectrum contains only the peak with m/z 1124, belonging to a single compound, namely, EMF Ce@C₈₂. The purity of the sample obtained is also confirmed by the chromatogram (see Fig. 5, inset). According to the data of HPLC and mass spectrometry, the purity of the isolated EMF Ce@C₈₂ was ~98%. Analogous results were obtained by the estimation of the purity of the EMF sample with yttrium (Fig. 6).



Fig. 3. HPLC chromatograms (Regis Buckyclutcher column, elution rate 12 mL min⁻¹, toluene as eluent) of fraction **B** (*a*), endohedral dimetallofullerene Ce₂@C₇₈ (*b*), and monometallofullerene Ce@C₈₂ (*c*).



Fig. 4. HPLC chromatograms (Regis Buckyclutcher column, elution rate 12 mL min⁻¹, toluene as eluent) of fraction A (*a*), endohedral dimetallofullerene $Y_2@C_{84}$ (*b*), and monometallofullerene $Y@C_{82}$ (*c*).

In addition to the pure samples of endohedral monometallofullerenes with cerium and yttrium, individual



Fig. 5. MALDI-TOF mass spectrum of positive ions of pure EMF Ce@C₈₂. The HPLC chromatogram (Cosmosil Buckyprep column, elution rate 18 mL min⁻¹, toluene as eluent) of pure EMF Ce@C₈₂ is shown in inset.



Fig. 6. MALDI-TOF mass spectrum of positive ions of pure EMF Y@C₈₂. The HPLC chromatogram (Cosmosil Buckyprep column, elution rate 18 mL min⁻¹, toluene as eluent) of pure EMF Y@C₈₂ is shown in inset.

dimetallofullerenes $Y_2@C_{84}$ and $Ce_2@C_{78}$ have been isolated for the first time in the second step of HPLC and characterized (Figs 7 and 8). The MALDI-TOF mass spectra of positive ions of dimetallofullerenes $Y_2@C_{84}$ and $Ce_2@C_{78}$ are shown in Figs 7 and 8 (inset). The spectra exhibit only the peaks with m/z 1186 and 1216 corresponding to the $Y_2@C_{84}^+$ and $Ce_2@C_{78}^+$ ions, respectively. According to the HPLC and MALDI-TOF data, purity of the isolated $Y_2@C_{84}$ and $Ce_2@C_{78}$ compounds was ~98%.

The absorption spectra of EMF are known to be very sensitive to the structure (symmetry) of the carbon cage. Metal atoms, such as yttrium, lanthanum, cerium, gado-linium, or holmium, inserted inside the carbon cage of the same symmetry exert a weak effect on the general character of the spectrum and insignificantly shift the positions of the characteristic bands (by 10–20 nm). The



Fig. 7. Absorption spectrum of pure EMF $Y_2@C_{84}$ in toluene. The MALDI-TOF mass spectrum of positive ions of pure EMF $Y_2@C_{84}$ is shown in inset.



Fig. 8. Absorption spectrum of pure EMF $Ce_2@C_{78}$ in toluene. The MALDI-TOF mass spectrum of positive ions of pure EMF $Ce_2@C_{78}$ is shown in inset.

spectra of the monometallofullerenes $M@C_{82}$ isolated by us agree with those described earlier.^{1,12} The absorption spectrum of dimetallofullerene $Y_2@C_{84}$ (see Fig. 7) contains a wide set of characteristic bands at 355, 482, 625, 710, and 785 nm and the absorption edge at 800 nm.

The absorption spectrum of dimetallofullerene $Ce_2@C_{78}$ in toluene with the characteristic bands at 387, 515, 555, and 637 nm and the absorption edge about 1000 nm is presented in Fig. 8. Dimetallofullerene $La_2@C_{78}$ has been isolated previously,¹³ and the ¹³C NMR spectroscopic data showed that the structure of the carbon cage of this molecule corresponded to the D_{3h} - C_{78} symmetry (78 : 5). The absorption spectrum of $La_2@C_{78}$ in carbon disulfide is similar to that of $Ce_2@C_{78}$ in toluene and contains an analogous set of characteristic bands with a slight shift (from 3 to 18 nm) at 386, 533, 561, and 647 nm and the absorption edge at 1000 nm. It can be

assumed that the Ce₂@C₇₈ compound isolated by us has the same structure of the carbon cage as the La₂@C₇₈ molecule: D_{3h} -C₇₈ (78 : 5).

The optimization of the conditions of preparation of the composite graphite electrodes and their vaporization in the electric arc made it possible to obtain the soot enriched in EMF. As a result, pure EMF M@C₈₂ (M = Y, Ce) samples were prepared and endohedral dimetallofullerenes $Y_2@C_{84}$ and Ce₂@C₇₈ have been synthesized for the first time, isolated, and characterized by MALDI-TOF, HPLC, and optical spectroscopy. The structure of the carbon cage for dimetallofullerene Ce₂@C₇₈ corresponding to the D_{3h} symmetry (78 : 5) was proposed.

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