New EPR signals of endohedral metallofullerenes

V. K. Koltover,* Ya. I. Estrin, V. P. Bubnov, and E. E. Laukhina

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: koltover@icp.ac.ru

The EPR spectra of endohedral metallofullerenes (EMF), La-EMF and Y-EMF, which were free of admixtures of C_{60} and of other empty fullerenes, were examined. Endohedral metallofullerenes were prepared by extraction of fullerene-containing soots with DMF. New signals with *g* factors close to those of fullerene radical anions were observed in the EPR spectra of solutions of EMF in DMF and DMSO. At ~20 °C, these signals are observed as a doublet ($\Delta H_{pp} \approx 0.04$ mT) and singlet ($\Delta H_{pp} \approx 0.01$ mT) in solutions of La-EMF and Y-EMF, respectively. These EPR signals belong to solvated La@C_{82} and Y@C_{82} molecules and are characterized by small hyperfine interaction constants a_M due to a substantial decrease in the spin density of the unpaired electron at the metal atom.

Key words: endohedral metallofullerenes, EPR, La@C_{82}, Y@C_{82}, solvates, molecular clusters.

Endohedral metallofullerenes (EMF) belong to a new class of compounds containing one metal atom (sometimes, two or three metal atoms) inside the fullerene C_{2n} cage. The C_{82}-containing compounds are the most stable endohedral metallofullerenes.[1-3] Endohedral monometallofullerenes (metal is lanthanide, yttrium, scandium, *etc.*) are paramagnetic.[1-9] Previously, it has been suggested that EMF be used for the construction of new materials[1-5] and oxygen sensors[6] as well as in NMR tomography.[10] Until recently, EMF have been difficultly accessible because standard procedures for their extraction from fullerene-containing soots afforded extracts containing no more than 2% of these compounds.[1-6] Hence, the physical and chemical properties of EMF, including radiospectroscopic properties, remain poorly studied. We developed a new procedure for the stepwise extraction and concentration of EMF, which makes it possible to obtain virtually pure compounds (free of admixtures of empty fullerenes) even at the stage of extraction without application of liquid chromatography.[7] Owing to this procedure, EMF became readily accessible in preparative amounts and can be studied comprehensively by physicochemical methods. In the present work, we describe new paramagnetic states of EMF, which have not been observed previously.

Experimental

The solvents used, *viz.*, *o*-xylene, *o*-dichlorobenzene (DCB), DMF, and DMSO, were purified by distillation, dried, and kept under an Ar atmosphere. Endometallofullerene soots were synthesized in an electric-arc reactor equipped with composite graphite electrodes containing metallic lanthanum or yttrium.[5] Endohedral metallofullerenes were extracted according to a two-step scheme by *o*-xylene (3 cycles) and DMF (1 cycle).[7] In each cycle, the soot (10 g) was shaken with a boiling solvent (250 mL) for 3 h. The resulting solution was filtered off, dried *in vacuo*, and weighed. After the first step of extraction, a portion (10 g) of the soot gave 0.13 g of the extract containing fullerenes C_{60} (~79%) and C_{70} (~20%) and EMF (~0.4%). After the second step of extraction, the same portion of soot yielded 0.10 g of the extract, which consisted virtually of EMF and did not contain empty fullerenes. All operations were performed under an Ar atmosphere.

The mass spectra were measured on a time-of-flight laser-ionization (MALDI) TOF-1 spectrometer (Germany) and on an Elektron spectrometer (Ukraine) using ionization with ^{252}Cf decay fragments. The IR spectra were recorded on a Specord M82 spectrophotometer (Karl Zeiss, Germany) according to a standard procedure (in KBr pellets). Elemental microanalysis was carried out by a standard technique. The EPR spectra were recorded on E-104A (USA) and Radiopan (Poland) spectrometers in the X range under conditions precluding distortion of the line shape. The saturated solutions of EMF in DCB, DMF, and DMSO were thoroughly filtered from the precipitate. The degree of dissolution of EMF was monitored by measuring the intensity of the EPR signal of the solution. Either prolonged storage (several weeks) at ~20 °C or heating (at 150 °C for ~10 min) of the solutions was required to attain equilibrium because the EMF powders dissolved rather slowly. In all experiments, "ripening" of solutions was carried out following thorough degassing by double freezing—evacuation *in vacuo* (~10^{-3} Torr) in sealed tubes. The EPR spectra of the solutions in DCB were recorded in standard quartz ampules with an outer diameter of 3 mm, which were placed into a Dewar quartz tube of a Varian temperature-controlled unit. The EPR spectra of the solutions in DMF and DMSO were measured in standard glass capillaries with an inner diameter of 1 mm, which were placed into a 3-mm quartz ampule filled with silicone oil as the temperature-controlling liquid.

Results and Discussion

The mass spectrum (Fig. 1) demonstrates that the DMF extract does not contain empty fullerenes. Thus, lines of C_{60}, C_{70}, and higher fullerenes are virtually absent. The most intense line belongs to La@C_{82}

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(m/z = 1123). However, lines belonging to molecular ions from La@C_{74} to La@C_{106} (at m/z from 1027 to 1411) are also observed. In the mass spectra of Y-EMF, C_{60} and C_{70} were also not detected, but the lines of Y@C_{82} and Y@C_{80} were observed (at m/z 1073 and 1049), the most intense line belonging to Y@C_{82}.

Electron paramagnetic resonance is employed as the major method for the identification of paramagnetic EMF.[1—9] Paramagnetism of La-EMF results from the fact that the La atom donates two 6s valence electrons and partially one 5d electron to the aromatic fullerene cage.[1,2] The spectrum of La-EMF dissolved in DCB (Fig. 2, spectrum *1*) is, in principle, similar to the spectra of solutions of La@C_{82} in standard solvents (in chlorobenzenes, toluene, *o*-xylene, or CS_2) reported previously.[1—8] This spectrum is characterized by a superposition of two octet signals, which partially overlap with each other (for example, the fifth and seventh components of the first signal overlap with the fourth and seventh components of the second signal, respectively). The octet structure of the spectrum appears due to hyperfine interaction between the unpaired electron and the magnetic moment of ^{139}La, whose nuclear spin (I) is 7/2.[1,2] The most intense octet in spectrum *1* (see Fig. 2) is characterized by a hyperfine interaction constant a_{La} = 0.115(±0.002) mT, and the second octet has a_{La} = 0.081(±0.004) mT. Since the width of the individual lines ΔH_{pp} = 0.0136(±0.0002) mT, *i.e.*, this value is substantially smaller than a_{La}, the octet hyperfine structure is well resolved. The octet signals in spectrum *1* (see Fig. 2) are completely identical both in shape and the hyperfine interaction constant to the signals of two isomers of La@C_{82} reported previously, which differ in the symmetry of the fullerene cage (C_2 and C_{3v}).[1,2] In these compounds, the hyperfine interactions are isotropic-contact in character and the small a_{La} value indicates that the unpaired electron of the La atom is delocalized over the C atoms of the fullerene cage.[1,2]

In addition to 16 lines of two major octet signals, spectrum *1* (see Fig. 2) has also several weak lines resulting from small admixtures of other La@C_{2n} and from the hyperfine structure at the ^{13}C nuclei (see, for example, Refs. 1, 2, and 4). The mass spectrum of the specimen shown in Fig. 1 has major lines of La@C_{82} along with weak lines corresponding to other La@C_{2n}.

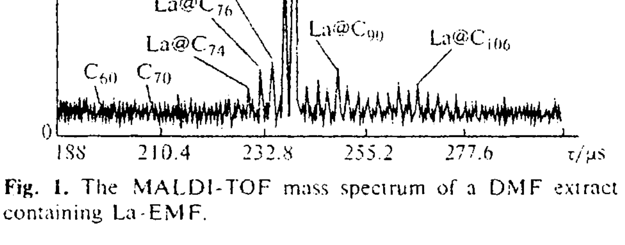

Fig. 1. The MALDI-TOF mass spectrum of a DMF extract containing La-EMF.

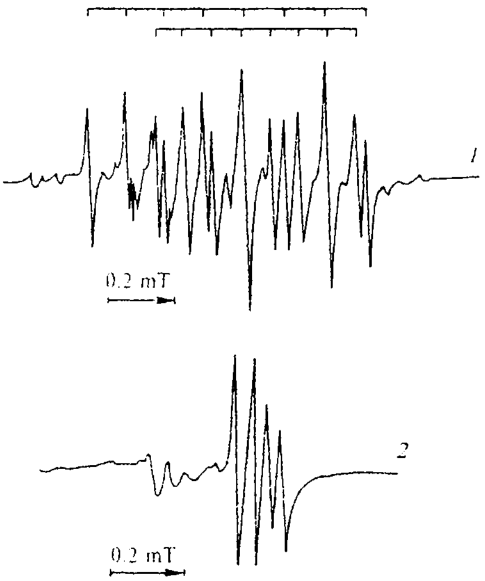

Fig. 2. EPR spectra of La-EMF (*1*) and Y-EMF (*2*) in DCB. The spectra were recorded in the absence of O_2 at 290 K. H_m = 0.0025 mT, P = 0.5 mW.

No fundamental differences are observed between our spectrum of Y-EMF in DCB (see Fig. 2, spectrum *2*) and those of this compound in DCB described previously.[3,9] Paramagnetism of Y@C_{2n} occurs due to the fact that the Y atom completely donates two 5s electrons and partially one 4d electron to the fullerene cage.[1,3] The major characteristic feature of spectrum *2* (see Fig. 2) is the presence of two well-resolved doublet signals with the hyperfine interaction constants a = 0.048(±0.002) mT (the more intense doublet) and 0.032(±0.002) mT (the lower intensity doublet). The characteristics of these signals correspond to those of the known signals of two different isomers of Ya@C_{82} with hyperfine structure at ^{89}Y (I = 1/2).[1,3] Yet another weak doublet signal at low field (a_Y = 0.05 mT) is, apparently, attributable to the isomer of Y@C_{80} whose line is also present in the mass spectra of our specimens along with the major line of Y@C_{82}.

Therefore, the data of EPR spectroscopy combined with the results of mass spectrometry prove that the method for extraction developed by us[7] enables one to prepare EMF analogous to those obtained previously according to traditional extraction schemes with the use of liquid chromatography, and yet in substantially larger amounts.

The EPR signal of La-EMF in DMF at ~20 °C (Fig. 3, spectrum *1*) occurs as a symmetric doublet with g = 2.001(2) and ΔH_{pp} = 0.039±0.002 mT. An analogous doublet signal is observed for a solution of this EMF in DMSO (g = 2.001(3), ΔH_{pp} = 0.043±0.002 mT). Therefore, the shapes of the signals of La-EMF in the above-mentioned solvents differ substantially from the standard octet signals of La-EMF in DCB.

Apparently, the peculiarities of the EPR signals of La@C_{82} in DMF and DMSO are associated with the specificity of solvation of EMF in these solvents. The EMF molecule possesses a dipole moment of 3—4 D because a position shifted toward the C_{82} carbon cage is energetically more favorable for the metal atom than that in the center of the fullerene cage.[1] Hence, Coulomb interactions of EMF with DMF and DMSO should be stronger than those with DCB (the dipole moments of these solvent molecules are 3.86, 3.96, and 2.5 D, respectively). According to the elemental analysis data, the DMF extracts contained N (2.5%), belonging, apparently, to DMF molecules, along with La (11.8%) and C (82.3%). Our results suggest that, on the average, two DMF molecules per La@C_{82} molecule are present in the initial DMF extract. In addition, the IR spectra of the DMF extracts of La-EMF have absorption bands typical of stretching (2925 and 2854 cm^{-1}) and deformation (1387 cm^{-1}) vibrations of the Me groups of DMF along with the stretching vibration band (1652 cm^{-1}) of the carbonyl group. The latter band is shifted by 20 cm^{-1} compared to that of pure DMF (1672 cm^{-1}), which is indicative of rather strong interactions between EMF and DMF.

We believe that the doublet EPR signal is actually a poorly resolved octet signal from La@C_{82} molecules solvated by the solvent molecules. Analogous quasi-doublet patterns of the EPR spectra appear, for example, in the case of the occurrence of a mechanism of broadening of individual lines to the value comparable with the hyperfine interaction constant. Then, the hyperfine structure can be distorted in such a way that only two extreme lines of the "antiphase doublet" remain in the spectrum (see, for example, Ref. 11).

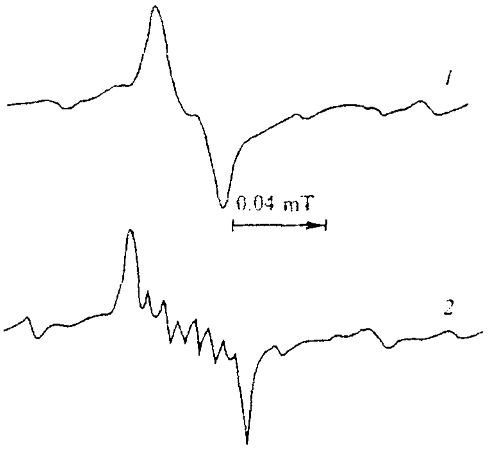

Fig. 3. EPR spectra of La-EMF in DMF after heating of the solution (10^{-3} Torr) at 150 °C for 30 min. The spectra were recorded in the absence of O_2 at 295 K (*1*) and 215 K (*2*): H_m = 0.002 mT, P = 0.5 mW.

An analogous doublet EPR signal was observed in solutions of Lu@C_{82} in toluene and some other low-polarity solvents in which standard octet spectra were obtained for La@C_{82}.[12] In the case of Lu@C_{82} (like ^{139}La, the major ^{175}Lu isotope has the nuclear spin of 7/2), the poor resolution of the octet hyperfine structure is attributable to substantial broadening of the spectral lines. The authors believed[12] that the lines are broadened because the ^{175}Lu nucleus possesses a large quadrupole moment whose interaction with the gradient of the intramolecular electric field substantially accelerates nuclear spin relaxation. However, the quadrupole moment of the ^{139}La nucleus is 25 times smaller than that of ^{175}Lu.[12] It is hardly probable that the gradients of the intramolecular electric field in La@C_{82} solvated by DMF or DMSO are higher than that in La@C_{82} solvated by DCB. Broadening of the spectral lines can, in principle, result from deceleration of rotational diffusion of the paramagnetic molecule, but this factor has a substantial effect only in highly viscous media.[13]

In the case under consideration, a decrease in the hyperfine interaction constant rather than the broadening of lines with hyperfine structure is the most probable reason for the poor resolution of the spectrum. A comparison of the distances between the extreme lines in the octet spectrum of La@C_{82} in DCB (Fig. 2, spectrum *1*) and in the "doublet" spectrum of the solution in DMF (Fig. 3, spectrum *1*) demonstrates that the a_{La} value in the second case is an order of magnitude smaller. The general theory of EPR spectra assumes[11] that the constant of the contact hyperfine interaction is proportional to the spin density of the unpaired electron on the nucleus. Therefore, a decrease in the a_{La} value signifies a decrease in the spin density on the La nucleus in solutions of La@C_{82} in DMF or DMSO compared to those in its solutions in DCB, toluene, or other standard solvents.

This interpretation of the "doublet" signal is also confirmed by a comparative analysis of the saturation curves of the signals of La-EMF. Since the major mechanism of spin-lattice relaxation involves modulation of hyperfine interactions upon collisions of EMF molecules,[14] a decrease in the spin density on the La nucleus should lead to saturation of the EPR signal even at a relatively low microwave power (P/mW). Actually, the "doublet" signal is characterized by the lower $P_{1/2}$ value (0.13 mW at 290 K) compared to that of the octet signal of La@C_{82} in DCB at the same temperature (0.8 mW).

The fact that the g factors of EMF are similar to those of fullerene radical anions indicates that the unpaired electron is delocalized over the fullerene cage.[1—2]

It can be seen in Fig. 3 that the distance between the extreme lines of the "doublet" increases as the temperature decreases. The temperature dependence of the hyperfine structure is reversible. This result agrees with our explanation taking into account that the electron transfer from the M atom to the fullerene cage requires an activation energy. The lower the temperature, the less

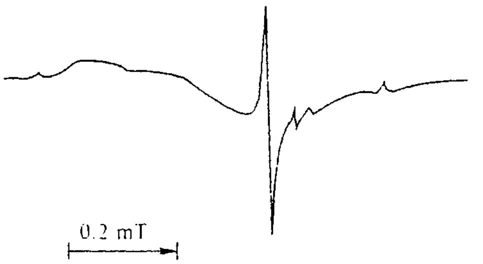

Fig. 4. EPR spectrum of Y-EMF in DMF (10^{-3} Torr) after heating of the solution (10^{-3} Torr) at 150 °C for 10 min. The spectrum was recorded in the absence of O_2 at 290 K, H_m = 0.002 mT, P = 0.5 mW.

probable this transfer and the higher the spin density on the M atom. Correspondingly, the a_{La} value and the distance between the extreme lines of the doublet increase. Moreover, due to an increase in the a_{La} value, the octet hyperfine structure (see Fig. 3, spectrum *2*, $a \approx 0.006(3)$ mT) becomes observable in the spectra recorded at low temperature.

The low-intensity satellite lines, which are observed to the right and left of the major "doublet" (see Fig. 3), belong, most likely, to other La@C_{2n} species, which are present as admixtures (La@C_{74}, *etc.*; see the mass spectrum shown in Fig. 1), and also, probably, to other isomers of La@C_{82}. The low intensities of the signals of the latter along with the small a_{La} value lead to distortion of the hyperfine structure giving rise to a singlet line.

Analogous results were obtained in experiments with yttrium-containing EMF. Unlike the spectra of solutions of Y@C_{82} in DCB, which have standard doublet signals, the spectrum of a solution in DMF has a narrow singlet signal with g = 2.001(3) and ΔH_{pp} = 0.012±0.002 mT (Fig. 4). The saturation curve of this signal is characterized by $P_{1/2}$ = 0.07 mW, whereas the doublet signal of Y@C_{82} in DCB at the same temperature has $P_{1/2} \approx 0.8$ mW. As in the case of the lanthanum-containing EMF, the new signal can be assigned to solvated molecules of the yttrium-containing EMF, and the singlet form of this signal (instead of the "doublet" form observed in the case of La@C_{82}) is attributable to the substantially smaller a_Y value compared to a_{La}. In the case of higher amplitudes of modulation of the magnetic field, a singlet signal at low field ($\Delta H_{pp} \approx$ 0.3 mT) is also observed. Apparently, this signal belongs to molecular clusters of EMF (see Fig. 4).

According to the data of EPR spectroscopy and quantum-chemical calculations, EMF have the formal $M^{3+}@C_{82}{}^{3-}$ electronic structure (a "superatom" with a positively charged metal nucleus and a negatively charged electron shell).[1,2] The unusually small a_M constants in solutions of EMF in DMF and DMSO suggest that the electron spin density is partially shifted from the C_{2n} core to the molecule of the solvation shell. However, additional experiments are required to confirm this suggestion.

To summarize, the procedure developed by us for the extraction of EMF from fullerene-containing soots[7] made it possible for the first time to prepare concentrated solutions of these compounds free of C_{60} and C_{70}. Solvates of empty fullerenes are known and are extensively studied, but no solvates have been observed previously in EMF solutions.[15]

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