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Spectral study of reactions of La@C_{82} and Y@C_{82} with amino-containing solvents

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A solvent effect on the electronic absorption UV-VIS and ESR spectra of La@C_{82} and Y@C_{82} was found. The UV-VIS spectra of La@C_{82} in pyridine, dimethylformamide, and hexamethylphosphorotriamide are identical with that of the La@C_{82}^- anion, which is evidence for La@C_{82} reduction in these solvents. In amino-containing solvents, the shape of the ESR spectra depends on the temperature and the time of preparation of the solutions. Changes in the ESR spectra of La@C_{82} and Y@C_{82} in dimethylformamide are due to functionalization of these compounds upon reduction.

Key words: endohedral metallofullerenes, ESR spectroscopy, reduction, amino-containing solvents, electronic absorption spectra.

Spectral data play an important role in studying the electronic structure of M@C_{82}. Nonpolar or weakly polar solvents usually have no noticeable effect on the spectral parameters. At the same time, the dipole moment of these molecules suggests an influence of the solvent polarity on their properties.

Comparison of the ESR spectra of a DMF extract of carbon black in *o*-dichlorobenzene (ODCB) and DMF showed their sharp distinction.[1,2] The spectrum in ODCB is a superposition of two octets from the topoisomers of La@C_{82},[3,4] whereas the lines of these octets are absent from the spectrum in DMF.

The preparation of solutions of endohedral metallofullerenes is usually associated with heating. Analysis of the spectra showed that solvents containing the amino groups chemically interact with La@C_{82} and Y@C_{82}.

In this work, we studied the electronic absorption spectra of L@C_{82} in carbon disulfide, ODCB, DMF, pyridine (Py), and hexamethylphosphorotriamide (HMPA) and the ESR spectra of La@C_{82} and Y@C_{82} in DMF and various mixtures of solvents.

Experimental

Procedures for the synthesis and purification (98%) of M@C_{82} have been described previously.[5] Solutions for ESR measurements were prepared in evacuated ampules (less than milligram of M@C_{82} in 1 mL of a solvent were taken). Heating was carried out at different temperatures for several hours. Electronic absorption spectra were recorded on a Hitachi U-2000 spectrometer. ESR spectra were obtained on a Varian E-12 A spectrometer equipped with a double cavity (8.8—9.3 GHz). A thermal stabilizer Radiopan (Poland) was used to study the temperature changes in spectra.

Both fresh samples of the complexes and those stored in air at room temperature were studied. The quality of the samples on storing was checked by the spectra in 1,3,5-trichlorobenzene (TCB). No effect of the storage conditions on experimental results was observed.

Results and Discussion

The hyperfine coupling constants a_{La} = 1.15 G and a_Y = 0.48 G correspond to the topoisomers of La@C_{82} and Y@C_{82} in nonpolar solvents.[3,4]

The electronic absorption spectra of solutions of La@C_{82} in DMF, Py, and HMPA differ from those in CS_2 and ODCB and coincide with the spectrum of the La@C_{82}^- anion[6] (Fig. 1). The latter is related, most likely, to the reduction of the endohedral metallofullerene with the solvents indicated.

The ESR spectra of La@C_{82} and Y@C_{82} in TCB and toluene are independent of the temperature and the time of dissolution, whereas in DMF both these factors have a substantial effect. The spectrum of a solution of La@C_{82} in DMF prepared at 160 °C exhibits after 15 h an octet with the HFC constant a_{La} = 0.38 G and a g factor of 1.9999 instead of the standard octet with a_{La} = 1.15 G. In 5 h at 100 °C, we observe a superposition of two octets and a singlet (Fig. 2, curve *1*): the octet with the standard for La@C_{82} HFC constant a_{La} = 1.15 G (g = 2.0002) and the octet with a_{La} = 2.12 G (g = 2.0004, g factor of the singlet 2.0005). Further heating at

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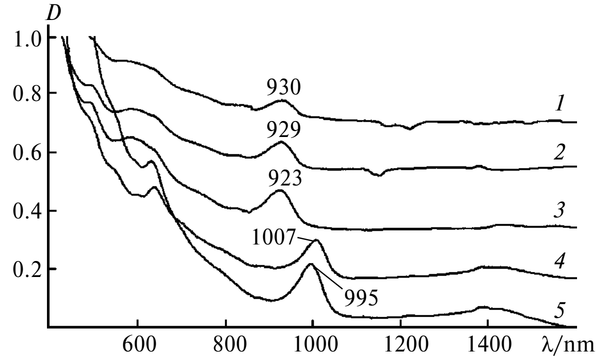

Fig. 1. Absorption spectra of La@C_{82} in the visible and near-IR regions in various solvents: HMPA (*1*), pyridine (*2*), DMF (*3*), CS_2 (*4*), and ODCB (*5*).

130—140 °C results in the disappearance of these two octets and the appearance of an octet with the HFC constant a_{La} = 0.38 G and several singlets in a low field. After heating for 15 h, the intensity of the octet increases and the singlet line between the second and third components of the octet disappears (Fig. 2, curve *2*). The total amplitude of the singlet lines after 30-h heating is 20% of the total amplitude of the octet. Visual comparison of the color intensity of the solutions and the ESR spectra of La@C_{82} in TCB (an almost colorless solution and an intense ESR spectrum) and in DMF (a dark-brown solution with a low-intensity ESR signal) indicates that the most part of the reaction products of La@C_{82} with DMF is diamagnetic.

The addition of toluene to a solution of the reaction products in DMF results in visible temperature changes in the shape of the spectrum. At room temperature the spectra of solutions in DMF—toluene mixtures (1 : 1; 0.5 : 1.5) did not differ from those in DMF. In a DMF—toluene (0.2 : 1.8) mixture, a single line is observed instead of the octet with a_{La} = 0.38 G. The temperature studies of a 1 : 1 mixture revealed no effect. In a mixture with a ratio of the components of 0.5 : 1.5, the amplitudes of the octet lines decrease reversibly and sharply in the 20—170 °C interval. A single line localized between the second and third octet lines appears and increases in intensity. The singlet is transformed into an octet on cooling the mixture with the component ratio 0.2 : 1.8 to −40 °C. Based on comparison of the amplitudes of the octet and singlet at different temperatures, we calculated the heat of equilibrium (~20 kcal mol^{-1}) between two forms of the reaction products. This product is, most likely, the polyfunctional derivative of La@C_{82}, whose solvation determines the spectral changes.

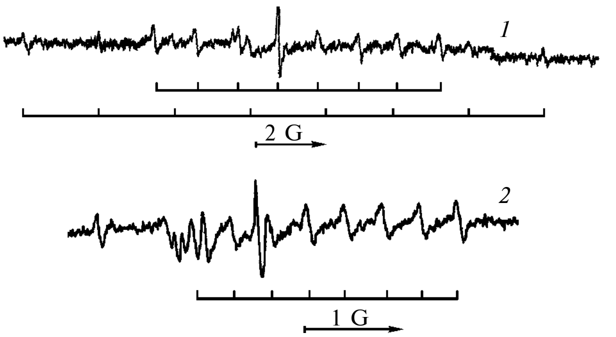

Fig. 2. ESR spectra of La@C_{82} in DMF recorded 5 h after heating at 100 °C (*1*) and 15 h after heating at 130—140 °C (*2*); corresponding spectra are also presented.

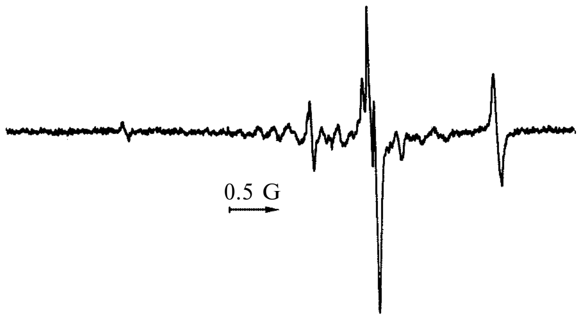

Fig. 3. ESR spectrum of Y@C_{82} in DMF after 4-h heating at 100 °C.

The shape of the ESR spectrum of Y@C_{82} in DMF also depends on the time and temperature. The ESR spectrum after 4-h heating at 100 °C (Fig. 3) contains ~15 single lines along with a doublet with a_Y = 0.05 G. The characteristic doublet of Y@C_{82} with a_Y = 0.48 G was not observed in the spectrum recorded immediately after heating of the solution.

The addition of DMF, Py, and HMPA to Y@C_{82} in TCB at room temperature resulted in the disappearance of the characteristic doublet and the appearance of a set of single lines and, in some cases, doublets with substantially lower HFC constants. The total intensity of new lines is always much lower than that of the initial doublet.

The observed transformations of La@C_{82} and Y@C_{82} are due, most likely, to the interaction of withdrawing molecules of endohedral metallofullerenes ($E_{1/2}$(La@C_{82}) = −0.48 V, $E_{1/2}$(Y@C_{82}) = −0.34 V) with donating molecules of solvents. At the same, large losses of the endohedral metallofullerene were not observed when La@C_{82} was extracted by dimethylformamide.[1,2,7] It can be assumed that a stable anion is the main reaction product of La@C_{82} with DMF.[6]

In connection with the reactivity of endohedral metallofullerenes, we have to mention the results of studying the photochemical reaction of C_{60} with triethylamine. The structure of this reaction product is explicable by a mechanistic scheme including successive electron and proton transfers, and radical recombination.[8] Within the framework of this scheme,[8] paramagnetic reaction products can have the M@$C_{82}H_nR_m$ structure, and the sum $n + m$ must be even. The variety of paramagnetic derivatives observed by the ESR spectra is related to a great number of groups of nonequivalent C atoms in the C_{82} fragment.

The obtained results show that the use of amino-containing solvents with technical and research purposes can lead, in some cases, to undesirable side transformations of M@C_{82}. It is most probably that during the extraction of M@C_{82} with amino-containing solvents the M@C_{82}^{-} anion is formed and oxidized in subsequent procedures to the resulting product M@C_{82}.

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