ESR spectra of products of oxidation of endometallofullerenes $M@C_{82}$ (M = Y, La, Ce, Gd)

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The ESR spectra of the products of oxidation of solutions and powders of $Y@C_{82}$ and $La@C_{82}$ with fuming sulfuric acid were studied. Based on the oxidation conditions and the sequence of spectral patterns, the spectra were attributed to the radical cations $M@C_{82}{}^{n+}$ (n = 2, 4), dimers $M^{3+}{}_2@C_{164}{}^{+}$, and polyendometallofullerenes.

Key words: endometallofullerenes, oxidation, ESR spectroscopy, radical cations.

Endohedral metallofullerenes $M_m@C_n$ attract great attention since their discovery[1] as representatives of a new class of molecules with unique topology in which one or several metal atoms are incorporated into the inner cavity of the carbon cage. The interaction between these components manifests itself as electron transfer from the metal to the carbon framework. The magnetic properties of $M@C_{82}$, *viz.*, diamagnetism or paramagnetism, are determined by the number of electrons (*viz.*, even or odd) of the M atom, the multiplicity of the M^{n+} ion in the $M^{n+}C_{82}{}^{n-}$ ion pair, and the type of interaction (*viz.*, ferromagnetic or antiferromagnetic) of electrons between M^{n+} and $C_{82}{}^{n-}$.

For this series of compounds, the oxidation state of the metal atom is accepted[2] to be 3+. The Y^{3+} and La^{3+} ions have non-zero electron spins, and the spins of Ce^{3+} and Gd^{3+} are 1/2 (one unpaired 4f electron) and 7/2 (seven unpaired 4f electrons), respectively.

According to the ESR data, $Y@C_{82}$ and $La@C_{82}$ have the spin $S = 1/2$ and g factor close to that of a free electron.[3,4] This implies that the spin of the $C_{82}{}^{\bullet 3-}$ cage is 1/2.

In the case of paramagnetic M^{3+} ions, one can expect either an increase or a decrease in the system multiplicity compared to that of M^{3+}, depending on the type of interactions of electrons between M^{3+} and $C_{82}{}^{\bullet 3-}$. An increase in the multiplicity can change the parameters of the fine structure of the ESR spectrum, and a decrease in the multiplicity can result in transition to the diamagnetic state.[5]

According to the data of measurements of the static magnetic susceptibility, $Gd@C_{82}$ possesses a high multiplicity[6] but its ESR spectrum was not observed at room temperature.[6,7] We were not able either to detect ESR spectra in the 77—300 K temperature interval for the $Ce@C_{82}$ and $Gd@C_{82}$ samples containing ~1 mg of the substance.

The $M@C_{82}$ complexes are scarcely soluble in CS_2, toluene, and chloro derivatives of benzene even after long heating. The dissolution of $La@C_{82}$ in amino-containing solvents (DMF, pyridine, and hexamethapol) is accompanied by reduction to the diamagnetic anion.[8,9] The true solubility of these compounds remains undetermined to date.

Endohedral metallofullerenes are polarographically oxidizable and reducible substrates. Only the first oxidation wave with a potential of ~0.1 V *vs.* ferrocene—ferricinium pair is known for them.[10] We can assume that +1 is not the limiting oxidation state for $M@C_{82}$.

Since no procedure for preparation of solutions with the known concentration of $M@C_{82}$ is available, the quantitative, the more so multistep oxidation of endometallofullerenes cannot be performed. For this reason, we chose fuming sulfuric acid as a one-electron oxidation agent. Varying its concentration, we attempted to synthesize the $M@C_{82}$ complexes with different oxidation states with the purpose to study their ESR spectra and obtain data on chemical transformations of $M@C_{82}$ accompanying oxidation.

The conditions of fullerene oxidation with fuming sulfuric acid affect the structure of the reaction products. The $C_{60}{}^{\bullet +}$ and $C_{70}{}^{\bullet +}$ radical cations were detected[11,12] by ESR in the oxidation of toluene solutions of C_{60} and C_{70}. When minor amount of the C_{60} crystals (~1 mg) was oxidized, the ESR spectrum of $C_{120}{}^{\bullet +}$ was recorded,[11,13]

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and the spectra of $C_{120}O^{\bullet+}$ and $C_{120}O^{\bullet\bullet 2+}$ were additionally detected during long oxidation (25 mg, 0.5 h). In the latter case, the IR spectrum of the isolated product showed[14] that ~40% polyfullerenes $(C_{60})_n$ are formed based on the C_{60} taken.

It was of interest to obtain evidence of the formation of polyendometallofullerenes upon the oxidation of $M@C_{82}$. The purpose of this work was to study the molecular and electronic structures of the products of oxidation of $M@C_{82}$.

Experimental

Procedures of the synthesis and purification (98%) of $M@C_{82}$ were described previously.[15] Two methods of oxidation were used. The first method was based on the reaction of $M@C_{82}$ in 1,2,4-trichlorobenzene (TCB) with a minor amount of fuming sulfuric acid containing ~20% SO_3. An evacuated ampule with a solution of $M@C_{82}$ (0.5 mL), whose spectrum was preliminarily recorded, was open, and an oxidant, *viz.*, droplet of fuming sulfuric acid or its emulsion in TCB was added. The reactants were stirred for several seconds, and recording the ESR spectra were begun.

In the second method, the $M@C_{82}$ powder (0.3—0.5 mg) was oxidized in an ampule by fuming sulfuric acid (0.3—0.5 mL).

ESR spectra were obtained on a Varian E-12A spectrometer with a double resonator. One resonator contained the sample under study, and the reference sample (Varian) with the *g* factor of 2.0028 (for the determination of the *g* factor of the paramagnetic species) was in another resonator. A Radiopan thermostatting system was used to study the temperature effect on the ESR spectra.

Results and Discussion

Spectra of $Y@C_{82}$ oxidation products. The ESR spectra of $Y@C_{82}$ in TCB (Fig. 1) consists of the central HFS doublet ($a_Y = 0.48$ G) and satellite lines belonging to the HFC with the ^{13}C atoms. Lines *1*, *5* and *1´*, *5´* are attributed to combinations of splittings $a_{^{13}C}$ and a_Y corresponding to $a_1 = 0.75$, $a_2 = 0.93$, $a_3 = 1.23$, $a_4 = 1.42$, and $a_5 = 1.88$ G. Weak lines *6*, *6´* and *7*, *7´* are the HFS components from the Y nuclei in the combined quartets $a_5 + a_1$ and $a_5 + a_2$ corresponding to the $Y@^{13}C_2{}^{12}C_{80}$ molecules.

The $a_{^{13}C}$ HFC constant in the ESR spectra of $M@C_{82}$ (M = Sc, Y, La) are close to each other due to the predominant localization of a lone electron on the fullerenes atoms of $C_{82}{}^{\bullet 3-}$.

The simulation of the ESR spectra of these compounds gave an estimate[16] of the number of C atoms in the groups corresponding to different HFC constants. In all compounds, eight magnetically equivalent C atoms correspond to the maximum HFC constant. We obtained the same result by the study of the integral ESR spectrum of $Y@C_{82}$ in which the ratio of intensities of the

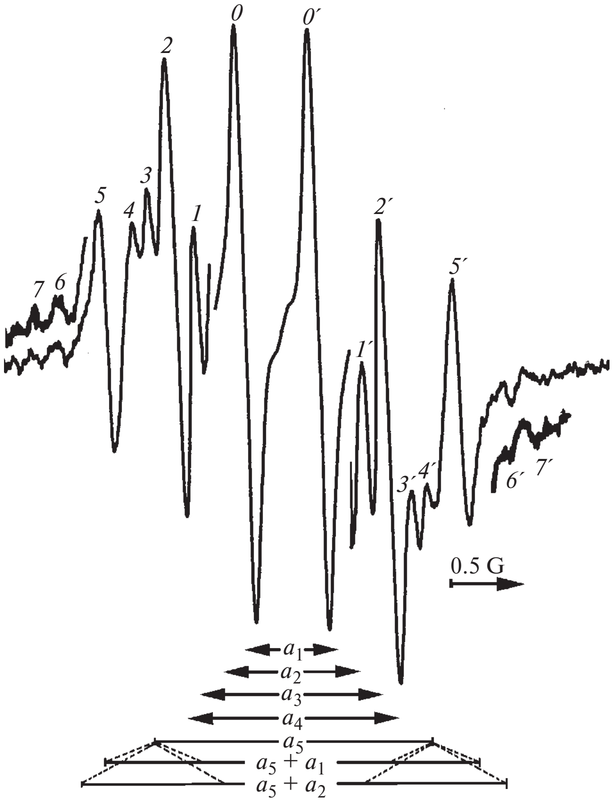


Fig. 1. ESR spectrum of $Y@C_{82}$ in TCB.

^{13}C satellite lines with the a_5 HFC constant to the intensity of the whole spectrum was determined.

Figure 2, *a* presents the ESR spectra recorded several tens of seconds after the addition of a fuming sulfuric acid droplet to a saturated solution of $Y@C_{82}$ in TCB. Curve *A* belongs to $Y^{3+}@C_{82}{}^{\bullet 3-}$ with an intensity of 1/30 of the initial one. Signal *A* was not found in the next spectrum recording after 60 s (Fig. 2, *b*). Curve *B* is a superposition of two doublets with different intensities attributing, most likely, to two different species of the $Y^{3+}@C_{82}{}^{\bullet -}$ type because this is the paramagnetic product closest to $Y^{3+}@C_{82}{}^{\bullet 3-}$ in the oxidation scheme. A similar pattern appears for the oxidation of $La^{3+}@C_{82}{}^{\bullet 3-}$ and will be discussed below. The more intense doublet is characterized by the constant $a_Y = 0.73$ G and *g* factor of 2.0026, and the less intensive doublet has $a_Y = 0.9$ G and $g = 2.0028$ (signal from $Y^{3+}@C_{82}{}^{\bullet 3-}$ has $g = 2.0005$). The intensity of curve *B* decreases to zero within several minutes.

A different pattern is observed when fuming sulfuric acid reacts with the $Y@C_{82}$ powder, which is rapidly dissolved, and the resulting spectra are rather intense.

When the spectra were recorded in the kinetic regime, the reaction between fuming sulfuric acid and $Y@C_{82}$ powder gave the spectral pattern, which was rather unchanged at room temperature indicating, perhaps, a higher oxidation state of the substrate.

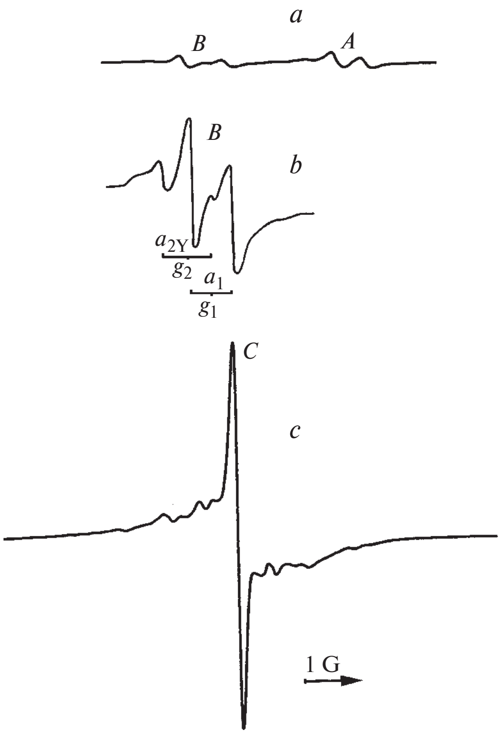


Fig. 2. ESR spectra of $Y^{3+}@C_{82}{}^{\bullet 3-}$ (*A*) and $Y^{3+}@C_{82}{}^{\bullet -}$ (*B*) recorded after a solution of $Y^{3+}@C_{82}{}^{\bullet 3-}$ in TCB was oxidized with fuming sulfuric acid (*a*), next recording of curve *B* after 60 s (*b*), and ESR spectrum of the primary product of oxidation of powder $Y^{3+}@C_{82}{}^{\bullet 3-}$ with fuming sulfuric acid (*C*) referred to $Y^{3+}@C_{82}{}^{\bullet +}$ (*c*).

The spectrum (*C*) of the paramagnetic species obtained by the dissolvation of Y@C_{82} in fuming sulfuric acid is presented in Fig. 2, *c*. Curve *C* does not contain the HFS from the Y nucleus but its HFC constants with the ^{13}C nuclei are high compared to those in the spectrum of Y@C_{82}: $a_1 = 0.6$, $a_2 = 1.2$, $a_3 = 1.95$, $a_4 = 2.4$, and $a_5 = 4.0$ G. For the Y@C_{82} complex the highest constant is $a_{13C} = 1.88$ G. The central linewidth in spectrum *C* is $\Delta H = 0.15$ G and $g = 2.0023$. The absence of the HFS from the Y nucleus can be attributed to either the low a_Y constant or decapsulation reaction

$$2\,Y@C_{82} + 3\,H_2SO_4 = Y_2(SO_4)_3 + 2\,C_{82} + 3\,H_2.$$

To prove that the endohedral structure remains unchanged at this oxidation state, we neutralized sulfuric acid with minor excess of triethylamine in a TCB solution. As a result, the colored solution decolorized, spectrum *C* disappeared, and a brown precipitate formed, whose broad signal had the *g* factor characteristic of the Y@C_{82} powder, and the ESR signal corresponding to Y@C_{82} was detected for the solution.

It can be assumed that spectrum *C* belongs to the next paramagnetic product of the stepwise $Y^{3+}@C_{82}{}^{\bullet +}$ oxidation. In this cation, the Y^{3+} ion should occupy the position corresponding to the minimum of the positive charge distributed over the C atoms of the $C_{82}{}^{\bullet +}$ radical cation. If the charge and spin densities are distributed in the radical cations in parallel, the low a_Y value can reasonably be explained.

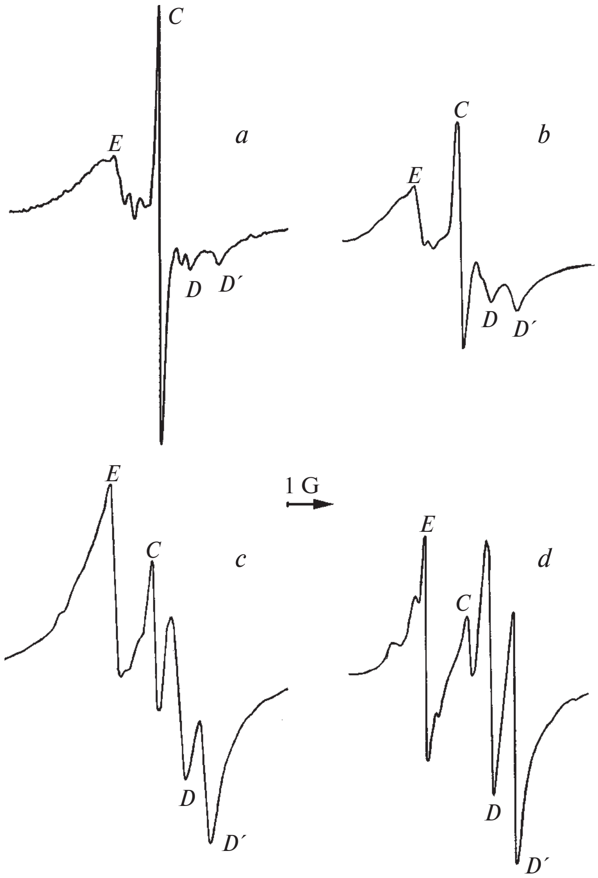


Fig. 3. ESR spectra of the products of oxidation of powder $Y^{3+}@C_{82}{}^{\bullet 3-}$ with fuming sulfuric acid recorded during the reaction: curves successively recorded after 10—15 s of heating to 60 °C (*a*—*c*) and curve at 60 °C (*d*).

After the ESR spectrum has been recorded, the further chemical transformations were carried out by short (10—15 s) heating to 60 °C. The intensity of line *C* decreased, and new lines appeared (see Fig. 3). It is noteworthy that the amplitudes of lines *D* and *D*′ are close to each other at different transformation stages, whereas the ratio of amplitudes of these lines to the amplitudes of lines *C* and *E* differs strongly. It can be assumed that lines *D* and *D*′ represent the HFS from the Y nucleus, *viz.*, a doublet with the constant $a_Y = 0.5$ G. The new lines *D*, *D*′ and *E* differ noticeably: $g_{DD'} = 1.9997$, $g_E = 2.0023$.

The *E* linewidth decreases noticeably with temperature. The spectrum in Fig. 3, *d* recorded at 60 °C exhibits satellite lines assigned, most likely to the ^{13}C HFS lines. A similar change in the linewidth has previously[11] been observed in the ESR spectrum of the $C_{120}{}^{\bullet +}$ radical cation.

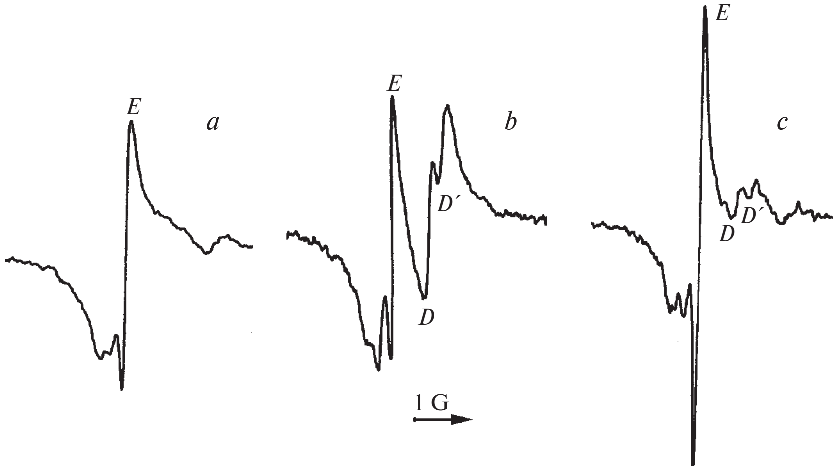
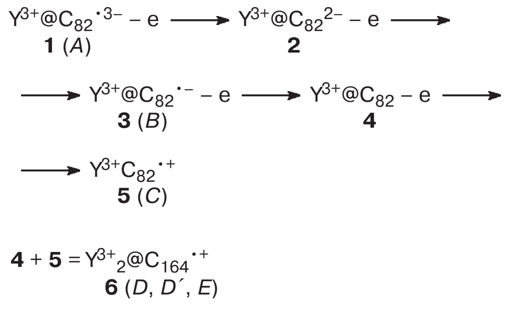


Fig. 4. Temperature dependence of the ESR spectra of the products of $Y^{3+}@C_{82}{}^{\bullet 3-}$ oxidation after keeping the sample for 5 days under standard conditions: 20 (*a*), 100 (*b*), 40 °C (*c*).

The intensity of lines *D* and *D′* at room temperature decreases in time more rapidly resulting in a relative increase in the intensity of line *E*. After 5 days, lines *D* and *D′* were absent, and line *E* was observed against the background of a broad signal. The temperature effect on the spectral pattern at this stage is presented in Fig. 4. Heating results in the appearance of lines *D* and *D′*, and at 100 °C their amplitudes become equal to that of *E*. The intensity of lines *D* and *D′* decreases sharply on cooling. Such a similarity in the reversibility of the spectral pattern shows that mutual transformations of labile reaction products occur in the system.

The number of individual ESR spectra detected in the oxidation of $Y@C_{82}$ exceeds the number the paramagnetic radical cations ($Y^{3+}@C_{82}{}^{\bullet -}$ and $Y^{3+}@C_{82}{}^{\bullet +}$). There are some grounds to ascribe spectra *E* and *D*, *D′* to different isomeric dimers $Y^{3+}{}_2@C_{164}{}^{\bullet +}$ formed according to Scheme 1.

Scheme 1



$$\underset{\mathbf{1}\,(A)}{Y^{3+}@C_{82}{}^{\bullet 3-}} - e \longrightarrow \underset{\mathbf{2}}{Y^{3+}@C_{82}{}^{2-}} - e \longrightarrow$$

$$\longrightarrow \underset{\mathbf{3}\,(B)}{Y^{3+}@C_{82}{}^{\bullet -}} - e \longrightarrow \underset{\mathbf{4}}{Y^{3+}@C_{82}} - e \longrightarrow$$

$$\longrightarrow \underset{\mathbf{5}\,(C)}{Y^{3+}C_{82}{}^{\bullet +}}$$

$$\mathbf{4} + \mathbf{5} = \underset{\mathbf{6}\,(D,\,D',\,E)}{Y^{3+}{}_2@C_{164}{}^{\bullet +}}$$

It can be assumed that the broad line in Fig. 4 is associated with the paramagnetic polyendometallofullerenes, which decompose to dimers on heating. The structure of the carbon framework in dimer **6** and analogous polyendometallofullerenes does not differ from that of fullerene dimers and polyfullerene. The stability of such oligomers is determined by the ratio of the Coulomb repulsion energy of the Y^{3+} cations and the energy of bridging C—C bonds. They can be stable only in an acidic medium in which the positive charges of Y^{3+} and $C_{82}{}^{\bullet +}$ are counterbalanced by the corresponding anions.

The structure of isomeric dimers **6** is determined by the position of the C atoms involved in binding of the endometallofullerenyl fragments. The theoretical calculations of the energy of formation of the isomeric C_{140} dimers showed that the dimers bound through the polar C atoms are most stable. The dimers in which polar atoms of one fullerenyl fragment are linked with the tropical atoms of another fragment are less stable. The dimers formed by the bonds of the tropical atoms are least stable.[17] When C_{70} is oxidized by fuming sulfuric acid, the ESR spectra of several isomeric $C_{140}{}^{\bullet +}$ radical cations were detected.[12]

The structure of dimers affects the position of the chemisorption sites of the Y^{3+} cations in the fullerenyl cages. The latter determines the value of the HFC constant a_Y.

Additional information on the structure of the dimers can be obtained from the difference in linewidths of *E* and *D*, *D′*. The shorter linewidth of *E* compared to those of *D* and *D′* can correspond to the linear structure of dimer **6** (long axes of ellipsoids are arranged on one straight line). The frequency of rotation of the linear dimer is higher than that of the dimer with the angular structure appeared by binding of polar and tropical atoms. The hindered rotation of the dimeric paramagnetic systems in fuming sulfuric acid, which affects averaging of the anisotropic interactions, has previously been found.[11,13]

Spectra of $La@C_{82}$ oxidation products. We failed to detect paramagnetic reaction products when $La@C_{82}$ was oxidized in a TCB solution with fuming sulfuric acid.

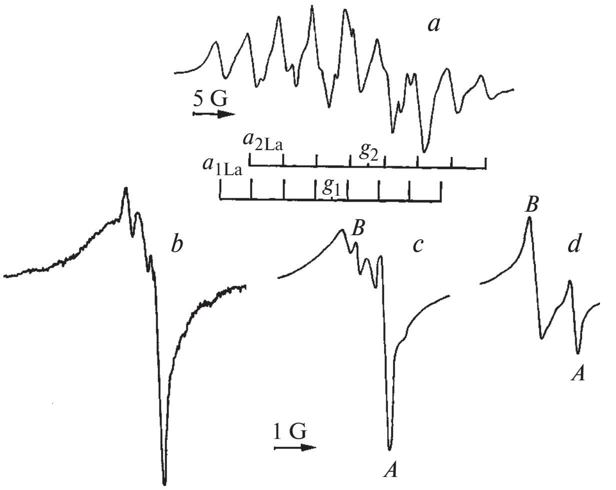


Fig. 5. ESR spectra of the products of $La^{3+}@C_{82}{}^{\bullet 3-}$ oxidation with fuming sulfuric acid: oxidation in TCB with an emulsion of fuming sulfuric acid (*a*), curve in the first minutes after the beginning of oxidation of the $La^{3+}@C_{82}{}^{\bullet 3-}$ powder with fuming sulfuric acid (*b*), after 10—15 s of heating to 40—60 °C (*c*), and upon repeat short heating (*d*).

However, the spectrum presented in Fig. 5, *a* was obtained upon oxidation with an emulsion of fuming sulfuric acid. This spectrum is a superposition of two octets with close splitting constant and difference of g factors approximately equal to the splitting on the La nucleus (in magnetic field intensity units). The reconstruction of the spectrum with the parameters $a_{1La} = 3.75$ G, $g_1 = 2.0053$, $a_{2La} = 4.0$ G, $g_2 = 2.0028$ is presented under the spectrum. The neutralization of sulfuric acid with triethylamine produces the spectrum of the initial La@C_{82}, *viz.*, octet with $a_{La} = 1.14$ G.

The appearance of two species close in spectral parameters upon the oxidation of Y@C_{82} and La@C_{82} in a TCB solution with fuming sulfuric acid is probably a result of the association of the cationic paramagnetic systems with the $SO_4{}^{2-}$ anions. The effect of association can be manifested both through the addition of the $SO_4{}^{2-}$ anions to $C_{82}{}^{\bullet -}$ by different manners and through dissociative equilibrium affecting the sites of preferential localization of the metal cation inside the cage.

The La@C_{82} powder is dissolved in fuming sulfuric acid more slowly than Y@C_{82}. For this reason, at the beginning of the reaction the ESR spectra of the oxidation products were detected against the background of a relatively broad singlet from the La@C_{82} powder.

The spectrum recorded in the first minutes of the reaction is presented in Fig. 5, *b*. The intense line *A* and two low-intensity lines in a lower field are detected against the background of the signal from the non-dissolved La@C_{82}. Short heating to 40—60 °C generates one more low-field line *B* (Fig. 5, *c*). Additional heating at 40—60 °C decreases the amplitude of signal *A*, increases the amplitude of signal *B*, and results in the disappearance of other signals (Fig. 5, *d*).

The paramagnetic species corresponding to signals *A* and *B* have different diffusion coefficients. Species of the second type are localized in the bottom part of the ampule where the La@C_{82} powder occurred, and the species of the first type are uniformly distributed over the whole solution bulk.

Based on the sequence of spectral patterns and the difference in diffusion coefficients, we assigned singlet *A* to $La^{3+}@C_{82}{}^{\bullet +}$ and line *B* to the $La^{3+}{}_2@C_{164}{}^{\bullet +}$ dimer.

If dimer formation is related to the reaction

$$La^{3+}@C_{82} + La^{3+}@C_{82}{}^{\bullet +} \longrightarrow La^{3+}{}_2@C_{164}{}^{\bullet +},$$

heterogeneity observed in the species distribution over the volume can be related to reactions near the surface of the La@C_{82} powder.

Oxidation of Ce@C_{82} and Gd@C_{82}. The spectra recorded during the oxidation of powders of these compounds have a comparatively low intensity and are constant in time, which allowed us to assign them to the products of oxidation of empty fullerenes, perhaps, present in the samples in minor amounts.

It can be assumed that the mechanism of M@C_{82} oxidation is the same for all metals, and the differences observed in the ESR spectra of the oxidation products are attributed to the paramagnetism of M^{3+} only or to its absence. It is most likely that the paramagnetism of the Ce^{3+} and Gd^{3+} ions and the interaction of these ions with the C_{82} cage in the paramagnetic states prevent the detection of ESR in the products of oxidation of Ce@C_{82} and Gd@C_{82}.

The results of studying the oxidation of Ce@C_{82} and Gd@C_{82} confirm the conclusion about the absence of fast decapsution reactions under the fuming sulfuric acid action. In the opposite case, the single spectral pattern would be observed regardless of the metal nature.

Thus, the study of the ESR spectra of the products of the interaction of Y@C_{82} and La@C_{82} with fuming sulfuric acid showed the formation of the intermediate forms $(M@C_{82})^{\bullet n+}$ (n = 2, 4) and radical cations of the isomeric dimers $(M^{3+}{}_2@C_{164})^{\bullet +}$. It was assumed that polyendometallofullerenes are formed in the acidic medium. The known mechanism of M@C_{82} reduction (depending on M, the number of polarographic waves is n = 4—6)[8] was supplemented by four oxidation steps.

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