ESR spectra of endohedral metallofullerene Ce@C_{82} radical anions in dimethylformamide and pyridine

S. P. Solodovnikov[a]★ **and S. F. Lebedkin**[b]

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: tuman@ineos.ac.ru
[b]Research Center of Karlsruhe, Institute of Solid State Nuclear Physics,
D-76021 Karlsruhe, Germany*

Endohedral metallofullerene Ce@C_{82} dissolved in dimethylformamide or pyridine is reduced to the radical anion. Analysis of hyperfine coupling with the topologically different ^{13}C nuclei indicates the electronic structure with bivalent cerium and the paramagnetic carbon framework Ce^{2+}@$C_{82}{}^{\bullet 3-}$. The ESR spectra of the radical anions of the functionalized Ce@C_{82} derivatives are detected.

Key words: endohedral metallofullerenes, ESR spectroscopy, reduction, nitrogen-containing solvents.

The recent study[1] of the optical absorption spectra of the endohedral metallofullerene La@C_{82} anions and cations has suggested that their oxidation and reduction occur inside the carbon cage. Although this conclusion seems evident for oxidation, we suppose somewhat different situation for reduction.

Unlike such "standard" solvents as benzene chloro derivatives, toluene, and CS_2, DMF and DMSO exert a pronounced effect on the shape of the ESR spectra of endohedral metallofullerenes La@C_{82} and Y@C_{82}.[2,3]

We have previously[4] shown that La@C_{82} is reduced by nitrogen-containing solvents to the anion. The reduction is accompanied by the functionalization of the endohedral metallofullerene. In this work, we studied the ESR spectra of the Ce@C_{82} radical anion.

Experimental

The procedures of synthesis and purification (98%) of M@C_{82} (M = Y, La, Ce, and Gd) have been described previously.[5] Solutions for recording ESR spectra were prepared in evacuated tubes (mg fractions of Ce@C_{82} in 1 mL of a solvent). Dissolution in DMF occurred for 2 weeks at ~20 °C, whereas in pyridine it took 7 h at 100 °C. Domestic solvents (analytical grade) and commercial DMF (Aldrich, 99%) were used.

ESR spectra were recorded with a Varian E-12 A spectrometer equipped with a double resonator (8.8—9.3 GHz). A Radiopan temperature stabilizer was used in studying the temperature dependences of the ESR spectra.

Results and Discussion

The standard ESR spectrum of the endohedral metallofullerene was measured after choosing the proper conditions (temperature, time of dissolution in DMF, amount of La@C_{82}).[4] The UV-VIS absorption spectra of La@C_{82} in DMF, pyridine, and hexamethylphosphotriamide[4] coincide completely with the spectrum of the anion obtained in Ref. 1. The shape of the spectra detected for La@C_{82} dissolved in DMF depends on both the dissolution rate, determined by the temperature and surface area of the endohedral metallofullerene powder, and the rate of chemical transformations, depending on the temperature and properties of the solvent.

Dimethylformamide is not a chemically neutral solvent. On heating it decomposes to dimethylamine and CO, and at ~20 °C its decomposition occurs by alkalis and bases.[6] Pyridine usually contains traces of various amines.[6]

The solubility of the endohedral metallofullerenes is very low. According to the rough estimate based on the measurement of the intensity of the ESR spectra, it is not higher than 10^{-4}—10^{-5} mol L^{-1}. For this reason, minor donor admixtures can be sufficient for both the reduction of the endohedral metallofullerene and formation of products of other reactions. The interaction of the endohedral metallofullerenes with the solvents under study cannot be unequivocally excluded. Minor amounts of individual topomers, which are presently accessible, do not allow this system to be studied in detail. However, the reductive properties of these solvents can be used to obtain new data on endohedral metallofullerenes. General concepts

---

* Forschungszentrum Karlsruhe, Institut für Nukleare Festkorperphysik, D-76021 Karlsruhe, Germany.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1052—1054, May, 2003.

about the mechanism of interaction of the latter (as electron acceptors) with donors (amines) can be elaborated on the basis of the results obtained in studying the properties of C_{60}. The mechanism of the photochemical reaction of fullerene C_{60} with triethylamine, which was established by studying the structure of the reaction product, includes three steps.[7]

In the first step, an electron is transferred from amine to the C_{60} molecule to form the $C_{60}{}^{\bullet -}$ radical anion. The second step includes the proton transfer from the CH_2 group of the triethylamine radical cation to the $C_{60}{}^{\bullet -}$ radical anion to form the $C_{60}H^{\bullet}$ radical, after which the chemical reaction is ceased by radical recombination in the reaction cage of the solvent.[7]

Depending on the properties of the couple including the endohedral metallofullerene and a reducing agent, different variants of this mechanism can occur.

In the case of the reaction of fullerene with triethylamine, various by-products can be formed along with the main product. The by-products are formed due to the escape of active species from the solvent cage at different steps of the mechanism. For example, at the first step, the $C_{60}{}^{\bullet -}$ radical anion can escape from the reaction cage, and the escape at the second step can provide the $C_{60}H^{\bullet}$ radical, which affords the $C_{120}H_2$ dimer, and the $(MeCH_2)_2N{-}CHMe^{\bullet}$ radical. The latter reacts with C_{60} to form the spin adduct and further the corresponding dimer.

In nitrogen-containing solvents, the UV-VIS absorption spectra correspond to the $La@C_{82}{}^{-}$ anion, and the ESR spectra are attributed to the functionalized endohedral metallofullerene derivatives.

Since the potentials of one-electron reduction of $La@C_{82}$, $Ce@C_{82}$, and $Gd@C_{82}$ differ only by 0.01 and 0.02 V,[8] we can assume that the mechanisms of their reactions with amines and solvents containing the amino groups are identical.

The electronic states of $Ce@C_{82}$ and $Gd@C_{82}$ differ from those for $La@C_{82}$ and $Y@C_{82}$ by multiplicity. The latter are low-spin complexes ($S = 1/2$), whereas the first two complexes have a high multiplicity.

The high multiplicity of $Gd@C_{82}$, which was established from the data of measurements of magnetic susceptibility,[9] is natural because the spin of Gd^{3+} is equal to 7/2 (the oxidation state of M^{3+} was accepted for the whole series of the metals under consideration). The high multiplicity of $Ce@C_{82}$, which was established by similar measurements,[10] is evidently related to the ferromagnetic type of interaction of one 4f electron with an unpaired electron of the C_{82} cage.

According to our data, no ESR spectra are observed in the 77—300 K interval for $Ce@C_{82}$ and $Gd@C_{82}$.[11] This is likely related to the properties characteristic of high-spin complexes, *i.e.*, the fine structure in the ESR spectra and a short time of spin-lattice relaxation.

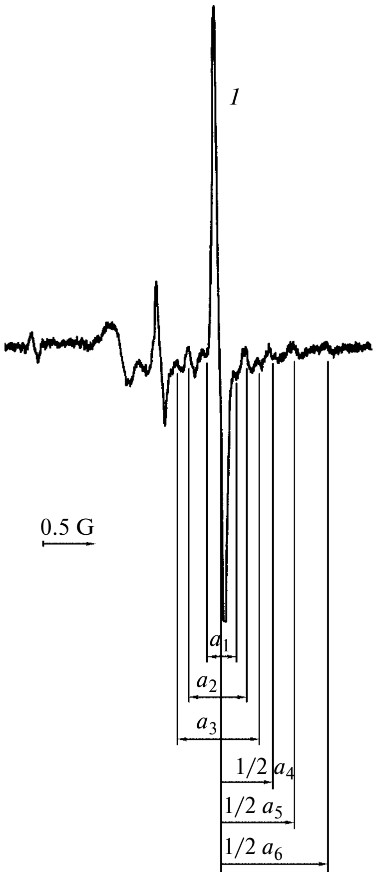

Fig. 1. ESR spectrum of the products of $Ce@C_{82}$ reduction in DMF.

The dissolution of $Ce@C_{82}$ and $Gd@C_{82}$ in DMF results in the appearance of similarly colored solutions. The ESR spectrum presented in Fig. 1 was recorded for the first solution, while the second solution gave no signal.

Evidently, all the lines in the spectrum belong to different low-spin species.

The carbon cage of C_{82} in $Ce@C_{82}$ consists of a set of topologically nonequivalent C atoms. For this reason, only the $Ce@C_{82}$ radical anion is a structurally individual species, unlike other functionalized paramagnetic endohedral metallofullerene derivatives, which are presented by a set of isomers. Therefore, the intensity of the ESR line of the radical anion should be much higher than those of other paramagnetic endohedral metallofullerene derivatives.

Line *1* in Fig. 1 is the most intense, which allows one to assign it to the radical anion.

An additional information confirming this conclusion is provided by the studies of the temperature plots of the linewidth. When the temperature increases from 20 to 70 °C, the width of line *1* decreases from 0.09 to 0.07 G, whereas the widths of other lines remain virtually unchanged. This effect is reversible with the temperature change. It is natural to assume that the radical anion is the most kinematically mobile species.

The $La@C_{82}^-$ anion is stable toward air oxygen.[1] The short contact of the sample, whose spectrum is presented in Fig. 1, with air results only in broadening of the lines due to paramagnetism of oxygen. The intensities of all lines remain unchanged after evacuation. Therefore, we can assume that all lines in this spectrum are attributed to different radical anions. These can be radical anions of the functionalized $Ce@C_{82}$ derivatives.

Analysis of the splittings between the HFS lines from the ^{13}C nuclei suggests some features of the electronic structure of the $Ce@C_{82}^{\bullet -}$ radical anion. The nuclei of the topologically different ^{13}C atoms are characterized by the following HFC constants: $a_1 = 0.25$, $a_2 = 0.50$, $a_3 = 0.75$, $a_4 = 1.00$, $a_5 = 1.40$, and $a_6 = 2.00$ G. They differ slightly from the HFC constants for the paramagnetic $M@C_{82}$ endohedral metallofullereness (M = Sc, Y, and La).[12]

The a_i values in this series are similar because the reduction extent of the carbon cage is the same (−3) and an unpaired electron in these compounds occupies the same orbital.

It stems from the aforesaid that in the $Ce@C_{82}^{\bullet -}$ radical anion the reduction extent of the carbon cage is −3, which implies the $Ce^{2+}@C_{82}^{\bullet 3-}$ charge distribution and, correspondingly, the low-spin state of the complex.

If the assumption on the reduction of the carbon cage is valid,[1] the distribution is different: $Ce^{\bullet 3+}@C_{82}^{4-}$. For the closed shell of C_{82}^{4-}, paramagnetism of the radical anion is determined by the $Ce^{\bullet 3+}$ cation ($4f^1$ electron), which is characterized by a higher anisotropy of the g factor and a short relaxation time.[13]

If line *1* in the spectrum (see Fig. 1) is attributed, in fact, to the radical anion, it should also be observed in the spectra obtained in other reducing media. The spectrum similar to that presented in Fig. 1 was detected for a solution of pyridine.

The difference in the ESR spectra of the cerium and gadolinium compounds in DMF can indicate that the reduction of the endohedral metallofullerenes does not result in decapsulation. This means a low probability of formation of the free $C_{82}^{\bullet 3-}$ radical trianion. The $Gd@C_{82}$ radical anion remains to be a high-spin complex and exhibits no ESR spectrum.

The ESR spectra of $Y@C_{82}$ and $La@C_{82}$ in DMF[4] differ from the spectrum of $Ce@C_{82}$ in the same solvent by a greater number of individual lines. This is related to the different natures of both the initial molecules and reaction products. In the first case, paramagnetic species are $M@HC_{82}R$ isomers (R is the NMe_2 group if DMF contains a sufficient amount of dimethylaniline).

In the case of $Ce@C_{82}$, only the $Ce@HC_{82}R^{\bullet -}$ radical anions, obtained from the precursors with the lowest reduction potentials, are paramagnetic species along with the radical anion of the endohedral metallofullerene itself. The isomers with the higher potentials are not reduced.

The reduction potential of C_{82} measured in pyridine[14] is higher than the reduction potentials of $La@C_{82}$ and $Y@C_{82}$ [8] in 1,2-dichlorobenzene. If this is not the artifact (due to the above data on pyridine), further studies of endohedral metallofullerenes are needed to resolve the obvious contradiction.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-33216) and the Ministry of Industry, Science, and Technologies (Contract 41.002.1.1415).

References

1. T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nagahata, X. Gao, E. Van Caemelbecke, and K. M. Kadish, *J. Am. Chem. Soc.*, 2000, **122**, 9316.
2. E. E. Laukhina, V. P. Bubnov, Y. I. Estrin, Y. A. Colod, M. A. Khodorkovskii, V. K. Koltover, and E. B. Yagubskii, *J. Mater. Chem.*, 1998, **8**, 893.
3. V. K. Koltover, Ya. I. Estrin, V. P. Bubnov, and E. E. Laukhina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 1765 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1745].
4. S. P. Solodovnikov, B. L. Tumanskii, V. V. Bashilov, S. F. Lebedkin, and V. I. Sokolov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 2141 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 2242].
5. S. Lebedkin, B. Renker, R. Heid, H. Schober, and H. Riettschel, *Appl. Phys. A*, 1998, **66**, 273.
6. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, 1988, 157; 267.
7. G. E. Lawson, A. Kitaygorodskiy, and Y. P. Sun, *J. Org. Chem.*, 1999, **64**, 5913.
8. W. Wang, J. Ding, S. Yang, and X.-Y. Li, in *Recent Advances in Chemistry and Physics of Fullerenes and Related Materials*, Eds. K. M. Kadish and R. S. Ruoff, 1997, **4**, 417.
9. H. Funasaka, K. Sugiyama, K. Yamamoto, and T. Takahashi, *J. Phys. Chem.*, 1995, **99**, 1826.
10. C. J. Nuttall, Y. Inada, K. Nagai, and Y. Iwasa, *Phys. Rev. B*, 2000, **62**, 8592.
11. S. P. Solodovnikov, B. L. Tumanskii, V. V. Bashilov, S. F. Lebedkin, and V. I. Sokolov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 928 [*Russ. Chem. Bull.*, *Int. Ed.*, 2002, **51**, 1009].
12. G. Seifert, A. Bartl, L. Dunsch, A. Ayuela, and A. Rockenbauer, *Appl. Phys. A*, 1998, **66**, 265.
13. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
14. M. R. Anderson, H. C. Dorn, S. Stevenson, P. M. Burbank, and J. R. Gibson, *J. Am. Chem. Soc.*, 1997, **119**, 437.

Received April 25, 2002;
in revised form December 18, 2002