Spectral properties of the C_{60} complex with dibenzenechromium

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The product of the interaction of fullerene C_{60} with dibenzenechromium (DBC) was studied by ESR and IR spectroscopy. The ESR spectrum contains a signal of the radical cation $DBC^{+\cdot}$. A signal of the C_{60}^{-} anion is virtually absent, which is most likely related to its broadening. The IR spectrum contains bands characteristic of the DBC^{+} cation in the (DBC)I molecule and four bands characteristic of C_{60}^{-}. The data obtained indicate the interaction of C_{60} molecules with the environment in the crystal structure of the complex.

Key words: fullerene C_{60}, radical ion salt, dibenzenechromium, IR spectra, ESR spectra.

Fullerenes are capable of forming ionic compounds with electron-donating organic and organometallic molecules.[1–6] Dibenzenechromium (DBC) is a strong electron donor with a potential ($E_{1/2}$ = –0.8 eV [7]) adequate for the reduction of C_{60} to C_{60}^{-}. In this connection, it can be used for the synthesis of ionic compounds of fullerenes, which has recently been demonstrated for the interaction of C_{60} with $Cr(arene)_2$, where arene is benzene, toluene, or mesitylene.[8,9] In this work, the product of the reaction of C_{60} with DBC was studied by ESR and IR spectroscopy.

Experimental

The $(DBC)C_{60}$ complex was obtained by the procedure described previously.[8] Fullerene C_{60} was reduced by dibenzenechromium in an argon atmosphere. A solution of DBC in benzene was added to a benzene solution of C_{60} with a reagent ratio of 1 : 1. The reaction occurs instantly, forming a fine black suspension. The reaction mixture was settled for 5 h. The precipitate was filtered off, washed with benzene and ether, and dried at 60 °C in an argon flow. Elemental analysis of the product showed that the DBC : C_{60} ratio is approximately equal to 1 : 1. Found (%): C, 86.06; H, 1.48; Cr, 5.6. $C_{72}H_{12}Cr$. Calculated (%): C, 93.1; H, 1.3; Cr, 5.6. The content of C is lower than the calculated value, which may be related to incomplete combustion of fullerene during analysis.[3] Similar results were obtained when toluene and mesitylene were used as solvents and at different starting ratios of DBC and C_{60} (from 1 : 1 to 5 : 1). The product is partially soluble in THF and DMSO and completely soluble in *N*-methylpyrrolidone.

Fullerenes C_{60} were obtained from the fullerene-containing soot by extraction with toluene followed by purification on graphite using liquid chromatography.[10] Commercially available DBC (Strem) was used. Solvents were distilled above sodium metal in an argon atmosphere.

IR spectra were recorded on a Specord IR-75 spectrophotometer. Samples were prepared in an inert atmosphere as a mixture with Nujol. ESR spectra were measured in an inert atmosphere as powders on an SE/X 2544 radiospectrometer (Radiopan, Poznan) at a UHF power of 2 mW and a magnetic field modulation of 0.032 mT within the 15—290 K temperature range.

Results and Discussion

Magnetic properties. ESR spectra of the powder and solution of the C_{60} complex with DBC at room temperature (Fig. 1) are similar to the spectra of the powder and solution of dibenzenechromium iodide. The only distinction is that the latter have no weak line with a *g* factor of 2.0000.

The ESR spectra of powders of the complex consist of a single line with a *g* factor of 1.986 and are not saturated at 100 mW in the 15—290 K temperature range. The width of this line for different samples of the complex varies within 2.5—4 mT and is almost tempera-

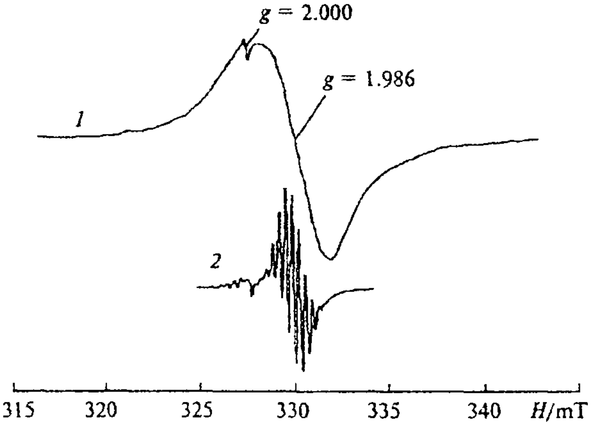

Fig. 1. ESR spectra of the C_{60} complex with DBC (1 : 1) at –20 °C: *1*, powder; *2*, solution in *N*-methylpyrrolidone.

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ture-independent within 15—300 K, the *g* factor being equal to that of dibenzenechromium iodide.[11] A very weak line with a *g* factor of 2.0000 and a width of 0.03 mT, characteristic of anionic compounds of C_{60}, is also observed (see, *e.g.*, Ref. 4 and literature cited therein). The nature of this line is discussed below. The ratio of the number of spins with *g* factors of 2.0000 to 1.986 estimated from the product of the line amplitude and the square of its width shows that the broad line of DBC contributes mainly (more than 99%) to the ESR spectrum of the powder of the complex.

The temperature dependence of the amplitude of the broad ESR line in the spectrum of the powdered complex at 15—290 K obeys the Curie law, which is valid for isolated spins undergoing weak interactions between each other and spins of the other type. Comparison of the second integrals of the ESR spectra of the powders of the complex and standard ($CuSO_4 \cdot 6H_2O$ powder) shows that in the temperature interval indicated, the number of spins in the complex is equal to $4.9 \cdot 10^{23}$ spins per mole of the complex, which is close to Avogadro's number.

The study of the C_{60} complexes with $Cr(arene)_2$ showed[9] that the ESR signal from the C_{60}^- monoanion is absent. The ESR spectra of the $(DBC)C_{60}$ powders exhibit a distinct anisotropy of the *g* factor, unlike the results of our work. The complexes with toluene and mesitylene are characterized[9] by the isotropic ESR spectra. Perhaps, these distinctions are due to the difference in the crystal structures, for example, because of different numbers of solvent molecules remaining in the sample.

The absence of the ESR signal attributed to C_{60}^- is explained, in our opinion, by the broad line width of C_{60}^-. The ESR spectrum of the anionic compounds of C_{60} depends substantially on the temperature, and at temperatures above 250 K, the main ESR signal of C_{60}^- is broadened (due to the Jahn—Teller perturbation) to such an extent that it cannot be observed. A narrow (with a width not broader than 0.1 mT and a *g* factor of 2.0000) signal appears, whose integral intensity is not higher than 25% of the total amount of C_{60}.[4] This signal has recently been assigned[12] to the product of interaction of C_{60} with oxygen, $C_{60}O_2^-$. In our case, the weak signal with $g = 2.0000$ is due, most likely, to minor admixtures of the $C_{60}O_2^-$ type, and the main signal of C_{60}^- is unobservable because of its broad width.

The ESR spectrum of a solution of the complex in *N*-methylpyrrolidone (see Fig. 1, spectrum *2*) is identical to that of a solution of (DBC)I. The ESR signal of C_{60}^- was not observed. Probably, the $(DBC)C_{60}$ complex decomposes in this solvent, and C_{60}^- reacts with the solvent to form diamagnetic products or a product with a broad ESR spectrum.

IR spectra. IR spectra of the $(DBC)C_{60}$ complex were recorded in an inert atmosphere as a suspension with Nujol, then the sample was opened, and its spectrum was measured in air. The IR spectrum of the $(DBC)C_{60}$ complex exhibits both bands which can be attributed to DBC and C_{60} and additional bands, some of which disappear after exposure to air, which is especially pronounced in the region of 650—700 cm^{-1} (Fig. 2). This indicates a strong sensitivity of the complex to oxygen.

The frequencies of absorption band maxima in the IR spectra of the DBC^+ cation (in dibenzenechromium iodide), C_{60}, and the complex of C_{60} with dibenzenechromium are presented in Table 1. The frequencies of the absorption band maxima of the DBC^+ cation correspond to the published data.[13,14] The IR spectrum of the neutral DBC molecule is presented in Table 1 for comparison.[12] The frequencies of metal—ligand vibrations in the 400—500 cm^{-1} region differ substantially for DBC and DBC^+ only. The spectrum of the $(DBC)C_{60}$ complex exhibits frequencies corresponding to the DBC^+ cation, which indicates the charge transfer between DBC and C_{60}.

The neutral C_{60} molecule is characterized[5,14,15] by four IR absorption bands at 527, 577, 1182, and 1428 cm^{-1}. In the spectrum of the C_{60}^- anion, the first two bands are weakly shifted,[6,15] and the band at 1182 cm^{-1} is not shifted in MC_{60} (M is an alkali metal) compounds,[15] but is shifted to 1179 cm^{-1} in C_{60} compounds with tetraphenylphosphonium halides.[6] The fourth band in the IR spectrum of C_{60}^- undergoes the

Table 1. Frequencies of absorption band maxima (ν/cm^{-1}) in IR spectra of DBC, (DBC)I, C_{60}, and the $(DBC)C_{60}$ complex

DBC	(DBC)I	C_{60}	$(DBC)C_{60}$
459	418 (0.8)		423 (2.3)
490	464 (0.54)		466 (1.6)
			521 (0.16)
		527 (1.0)	527 (0.43)
			543 (0.06)
		577 (0.4)	577 (0.12)
			617 (0.12)
			649 (0.08)
			677 (1.8)*
			686 (0.34)*
			696 (0.58)*
			731 (0.77)*
			767
795	794 (1.0)		792 (1.0)
			842 (0.22)
972	971 (0.38)		971 (0.46)
999	1003 (0.1)		1003 (0.5)
			1034 (0.32)*
			1078 (0.1)
			1142 (0.43)
		1182 (0.29)	1179 (0.09)
		1428 (0.24)	1405 (0.17)
1426	1430 (0.18)		1430 (0.72)
			1496 (0.01)*
3040	3033 (0.42)		3035

Note. The relative intensities of the maxima are presented in parentheses.

* The bands sensitive to O_2.

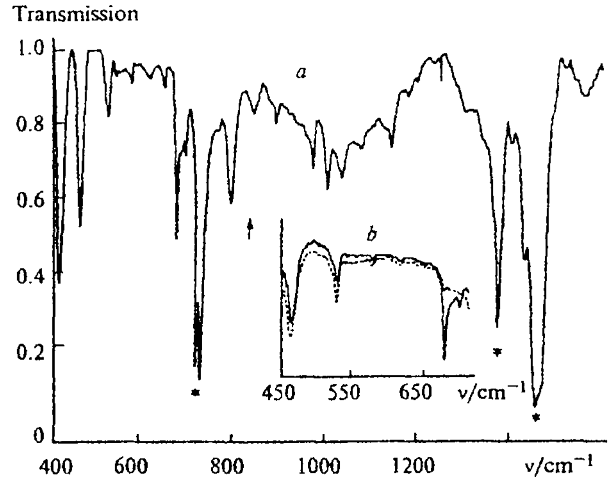

Fig. 2. *a.* IR spectra of the $(DBC)C_{60}$ complex in Nujol obtained in an inert atmosphere. The bands of Nujol are marked with asterisks. *b.* A part of the spectrum of $(DBC)C_{60}$ in an inert atmosphere (solid line) and after exposure to air (dotted line).

strongest shift: to 1394 cm^{-1} [6] and 1392 cm^{-1}.[15] In the spectra of the anionic compounds of C_{60}, the intensities of IR bands also change, the intensity of the band at 1400 cm^{-1} increasing most substantially.[6,15,16] The spectrum of the $(DBC)C_{60}$ complex exhibits bands at 527, 577, 1179, and 1405 cm^{-1}, which can be assigned to the anionic form of C_{60}.

Thus, the data of IR and ESR spectroscopy indicate the formation of the radical ion salt $(DBC)^+C_{60}{}^-$, whose IR spectrum exhibits somewhat less shift of the band at 1400 cm^{-1} than that of compounds with alkali metals[15] and tetraphenylphosphonium halides.[6] In addition, the absorption region of neutral C_{60} at 1428 cm^{-1} is hindered by the band of DBC^+ at 1430 cm^{-1}. The ratio of intensities of the bands attributed to C_{60} in the spectrum of $(DBC)C_{60}$ somewhat differs from that observed previously.[15,16] In particular, the ratio of intensities of the bands at 577 and 527 cm^{-1} is 1.5 times lower than that in the spectrum of C_{60}.[16] The relative intensities of the bands of DBC in the spectrum of $(DBC)C_{60}$ also differ somewhat from the intensities of the bands in the IR spectrum of (DBC)I.

The other specific feature of the IR spectrum of the $(DBC)C_{60}$ complex is the presence of a great number of bands (in particular, in the region of 600—800 cm^{-1}) in addition to those attributed to vibrations of DBC and the standard four bands of vibrations of C_{60}. This is most likely related to a decrease in the symmetry of the C_{60} molecule in the complex and the appearance of the forbidden vibrational modes. This decrease in symmetry can occur during the strong interaction of C_{60} molecules with neighboring molecules. In particular, adjacent $C_{60}{}^-$ anions can interact, for example, due to polymerization of C_{60} in the crystal structure. In fact, the appearance of additional IR bands in the region of 600—800 cm^{-1} has been observed in the spectra of polymerized fullerene C_{60}.[17] At the same time, the formation of polymeric charged chains of $C_{60}{}^-$ has been suggested in MC_{60} (M is an alkali metal) compounds[18] and in the structures of the C_{60} complexes with ditoluenechromium and CS_2.[9] Strong interaction between the C_{60} and DBC molecules, for example, due to the formation of structures with coordination of the η^2-type between the Cr atom in DBC and one of the C=C bonds in C_{60}, cannot be ruled out. The formation of similar C_{60} complexes with transition metals has previously been shown,[19—21] in particular, for vanadocene.[19]

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