The first complex of C_{60} fullerene with bis(ethylenedithio)tetrathiafulvalene radical cation: $C_{60} \cdot (BEDT—TTF \cdot I_3)$

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The complex of C_{60} fullerene containing the radical cation of the organic donor, *viz.*, $C_{60} \cdot (BEDT—TTF \cdot I_3)$, where BEDT—TTF is bis(ethylenedithio)tetrathiafulvalene, was synthesized for the first time. Single crystals of the complex were grown in benzonitrile. The crystals of this compound belong to the monoclinic system with a base-centered lattice. The unit cell parameters are as follows: a = 17.419(6), b = 9.997(4), c = 13.499(1) Å, β = 99.00 (1)°. The IR and electronic spectra of single crystals of the complex have absorption bands characteristic of the $BEDT—TTF^{\cdot+}$ radical cation and neutral C_{60}. The ESR spectrum has a signal with g = 2.0074 and ΔH_{pp} = 23 G belonging to $BEDT—TTF^{\cdot+}$. The position of the $I3d_{5/2}$ peak in the X-ray photoelectron spectrum confirms the formation of the I_3^- anion.

Key words: C_{60} fullerene; bis(ethylenedithio)tetrathiafulvalene; complexes of radical cations; electronic reflection spectra; XPS, IR, and ESR spectra.

A large number of donor-acceptor complexes with C_{60} fullerene have been synthesized,[1] some of which possess superconducting and ferromagnetic properties.[2,3] However, due to weak acceptor properties of fullerenes most organic donors form neutral complexes with C_{60}. In particular, complexes with tetrathiafulvalene derivatives were prepared, *viz.*, with bis(ethylenedithio)tetrathiafulvalene (BEDT—TTF),[4—6] dibenzotetrathiafulvalene,[7] octamethylenetetrathiafulvalene,[8] tetramethyltetraselenafulvalene,[9] tetramethylenedithiodimethyltetrathiafulvalene,[10] *etc.*[11,12]

It is known that tetrathiafulvalene derivatives are widely used for constructing radical-cation salts, which exhibit metallic and superconducting properties. For example, a series of superconducting radical-cation salts were prepared based on BEDT—TTF: $(BEDT—TTF)_2X$ ($X = I_3^-$, IBr_2^-, AuI_2^-, ReO_4^-, or $Cu(NCS)_2^-$) and $(BEDT—TTF)_4Hg_{2.89}Hal_8$ (Hal = Cl or Br).[13]

The C_{60} and C_{70} fullerenes form neutral complexes with BEDT—TTF. These complexes were prepared by cocrystallyzation of C_{60} or C_{70} and BEDT—TTF from carbon disulfide ($(BEDT—TTF)_2C_{60}$[4] and $BEDT—TTF \cdot C_{70} \cdot CS_2$[5]), toluene, benzonitrile ($(BEDT—TTF)_2C_{60}$[6]), or pyridine ($(BEDT—TTF)_2C_{60}(Py)_2$[5]).

A prerequisite for the manifestation of metallic conductivity or ferromagnetic properties in the complexes is their ionicity.[8] Previously, we have performed gas-phase intercalation of the $D_kC_{60}(Solv)_x$ compounds (where D is the donor and Solv is the solvent) with iodine to change the neutral state of molecular C_{60} complexes. In the course of intercalation, the solvent was replaced by iodine, which was accompanied by solid-phase oxidation of the donor to the radical-cationic or dicationic state to yield ternary systems $D_k^+ \cdot C_{60} \cdot I_n^-$ ($n > 5$).[14] However, the gas-phase intercalation is a diffusion process and the homogeneity of the resulting specimens is difficult to attain.

In the present work, we report the solution synthesis of the first ternary complex $C_{60} \cdot (BEDT—TTF \cdot I_3)$ containing the radical cation ($BEDT—TTF^{+\cdot}$).

Results and Discussion

The crystals of the $C_{60} \cdot (BEDT—TTF \cdot I_3)$ compound belong to the monoclinic system with a base-centered lattice. The unit cell parameters are as follows: a = 17.419(6) Å, b = 9.997(4) Å, c = 13.499(1) Å, β = 99.00(1)°. We performed indexing of all observed reflections. No systematic deviations from the monoclinic base-centered lattice were observed. Thus, there were three possible space groups, *viz.*, *C*2, *Cm*, or *C*2/*m*. In these unit cells, each fullerene molecule can have six neighboring C_{60} molecules located at approximately equal

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distances. In this case, two C_{60} molecules with the distances between their centers equal to 10.00 Å (the translational vectors are 0 ± 1.0) and four adjacent C_{60} molecules with the distances between their centers equal to 10.04 Å (the translational vectors are $\pm0.5\pm0.50$) can lie in the *ab* plane (Fig. 1). Hence, it can be suggested that the fullerene molecules form closely packed, slightly distorted layers parallel to the *ab* plane; the distances between these layers are 13.5 Å. The $BEDT—TTF^{\cdot+}$ radical cations and the I_3^- anions can occupy interlayer cavities. These layered structures are typical of C_{60} complexes with tetrathiafulvalenes. In these structures, the donor and solvent molecules are located between closely packed layers of the fullerene molecules.[8]

The IR spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ has absorption bands at 1429 and 1182 cm^{-1} characteristic of C_{60} (Fig. 2). The positions of these bands are identical with those in the spectrum of the initial fullerene, which is indicative of the absence of noticeable charge transfer to the C_{60} molecule. The spectrum has also absorption bands at 1384, 1289, 1021, 927, 899, 882, and 808 cm^{-1} characteristic of the $BEDT—TTF^{\cdot+}$ radical cation in the $BEDT—TTF \cdot I_3$ radical-cation salt (KBr pellets).[15] The intensity ratio and the positions of these absorption bands differ somewhat from those observed in the spectrum of $BEDT—TTF \cdot I_3$,[15] which may be associated with a change in the conformation of the $BEDT—TTF^{\cdot+}$ radical cation upon coordination with the spherical fullerene molecule. Changes in the conformation of the initially planar tetrathiafulvalene molecules were observed in all C_{60} complexes studied so far.[4—10]

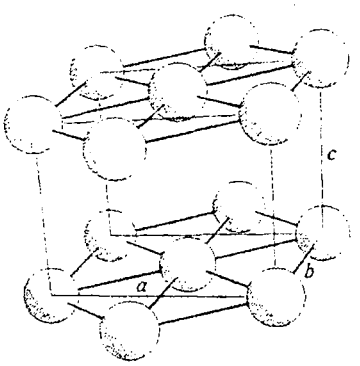

Fig. 1. Scheme of the arrangement of C_{60} molecules in the unit cell of $C_{60} \cdot (BEDT—TTF \cdot I_3)$. The C_{60} molecules are represented by balls. The crystallographic directions and the shortest distances between the centers of the C_{60} molecules are indicated by thin lines.

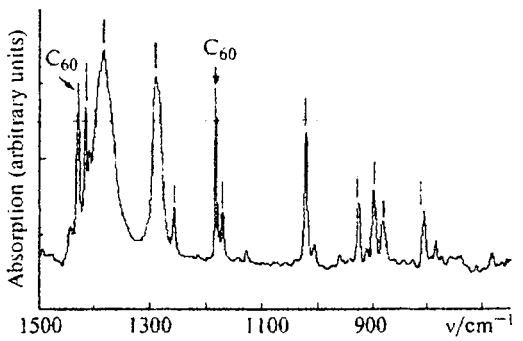

Fig. 2. IR spectrum of single crystals of $C_{60} \cdot (BEDT—TTF \cdot I_3)$. The absorption bands of the $BEDT—TTF^{\cdot+}$ radical cation and C_{60} fullerene are marked.

The electronic polarized reflection spectra of single crystals of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ were measured from the developed crystal face using three polarizations, *viz.*, two mutually perpendicular polarizations in the spectral range of 4.5—1.1 eV and one intermediate polarization (at an angle of 45° to polarizations *1* and *3*) in the range of 4.5—1.35 eV (Fig. 3). The polarized reflection spectra of the crystal of pure C_{60} in the region of 4.5—1.1 eV (the spectrum is isotropic and coincides with the published data[16]) and of the crystal of the $(BEDT—TTF)_2I_3$ radical-cation salt[17] were used for comparison.

The reflection spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ in three measured polarizations has peaks at 4.2, 3.6, 2.5, and 1.1 eV and a relatively weak peak at 1.96 eV, whose intensity is substantially lower in polarization *2* (see Fig. 3). It can be seen that the reflection spectra of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ are superpositions of the spectra of pure C_{60} and the $BEDT—TTF^{+\cdot}$ radical cation. In the spectrum of the complex, the positions of the peaks of fullerene (at 4.3 and 3.5 eV) are close to those in the spectrum of pure C_{60}, but in the former case, the peaks are noticeably broadened. Previously, broadening of the bands of C_{60} has been observed upon intercalation of fullerene complexes with iodine.[14] It is known that the reflection band at 2.4 eV in the spectrum of C_{60}[16] is associated primarily with the intermolecular LUMO—HOMO electron transfer between adjacent C_{60} molecules.[18] Hence, the intensity of this absorption should depend on the distance between the fullerene molecules. For example, this absorption band is absent in the spectra of complexes with isolated C_{60} molecules [19] or in the spectra of solutions of C_{60}.[20] In the case under consideration, the intensities of the bands at 2.5 eV in

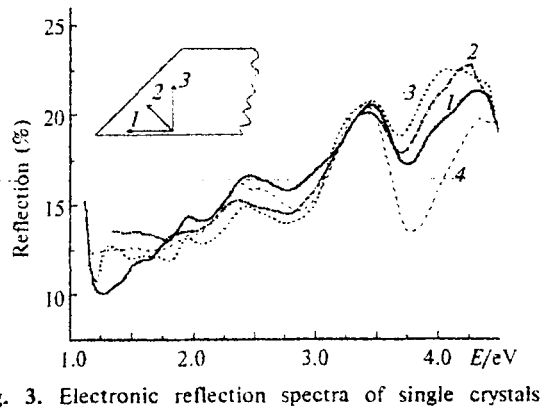

Fig. 3. Electronic reflection spectra of single crystals of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ measured from the developed face in three polarizations (*1*, *2*, and *3*) and the reflection spectrum of the crystal of the initial C_{60} (*4*).

the spectra of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ and pure C_{60} are approximately equal, *i.e.*, the distances between the adjacent C_{60} molecules in the $C_{60} \cdot (BEDT—TTF \cdot I_3)$ complex and in the crystals of initial C_{60} have similar values, which is consistent with the X-ray powder data.

A weak polarized band in the reflection spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ at 1.96 eV can be assigned to symmetry-forbidden electron transitions in C_{60} because the absorption spectrum of the initial C_{60} also shows weak absorption at 2 eV associated with symmetry-forbidden LUMO—HOMO transitions.[18] An increase in the intensity of this band compared to that of the initial C_{60} may be due to distortion of the icosahedral symmetry of the C_{60} molecules in the complex upon coordination with the $BEDT—TTF^{\cdot +}$ radical cation.

A reflection band is observed at 1.1 eV, which can be assigned to $BEDT—TTF^{\cdot +}$. This band is weakly polarized and the highest intensity is observed in polarization *1* (see Fig. 3). An analogous band was observed in the polarized spectra of single crystals of $(BEDT—TTF)_2I_3$.[17]

Reflection bands at 2.8—3.0 eV characteristic of the I_3^- anion[17] are absent in the spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$. Probably, these bands either are masked by more intense reflection bands of C_{60} or are not manifested in the measured polarizations.

The half-widths and the positions of the C1s, S2p, and $I3d_{5/2}$ peaks in the X-ray photoelectron spectra of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ are given in Table 1. On going from BEDT—TTF to $C_{60} \cdot (BEDT—TTF \cdot I_3)$, a positive shift of the S2p binding energy (E_b) is observed, which corresponds to a decrease in the electron density on the S atoms on going from the neutral BEDT—TTF compound to the radical-cationic state in $C_{60} \cdot (BEDT—TTF \cdot I_3)$.

The position of the $I3d_{5/2}$ peak with E_b = 619.4 eV in the compound under study is close to that for $(BEDT—TTF)_2 \cdot I_3$.[21] This is indicative of the fact that the specimen under study contains iodine as the I_3^- anion. The I^- anion is characterized by a substantially lower bond energy, for example, E_b = 617.7 eV in the compound $(Ph_4P^+)_2C_{60} \cdot (I^-)$.[23]

The ESR spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ (at room temperature) has an intense signal with g = 2.0074 and ΔH_{pp} = 23 G corresponding to the $BEDT—TTF^{\cdot +}$ radical cation. As the temperature decreases, the position and the width of the signal remain virtually unchanged (g = 2.0074 and ΔH_{pp} = 20 G at 77 K). However, the $(BEDT—TTF)_2I_3$ salts are characterized by noticeable narrowing of the ESR signal as the temperature decreases. For example, the β-$(BEDT—TTF)_2I_3$ salt gives the ESR signal with ΔH_{pp} = 18—24 G (300 K) and ΔH_{pp} = 2 G (5 K) and the θ-$(BEDT—TTF)_2I_3$ salt gives the ESR signal with ΔH_{pp} = 60—80 G (300 K) and ΔH_{pp} = 28 G (108 K).[13] The initial $BEDT—TTF \cdot I_{3.4}$ compound is characterized by the ESR signal with g = 2.0043 and ΔH_{pp} = 25 G (300 K), whose parameters also change as the temperature decreases (g = 2.0059 and ΔH = 10 G at 77 K).

The integrated intensity of the signal in the spectrum of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ increases by a factor of 2.2 as the temperature decreases from 300 to 77 K, which is attributable to localization of the electron on the $BEDT—TTF^{\cdot +}$ radical cation.

The conductivity of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ is $2 \cdot 10^{-4}$ Ohm^{-1} cm^{-1} (pressed pellets). This value is two orders of magnitude larger than the conductivity of the $(BEDT—TTF)_2C_{60}$ complex (10^{-6} Ohm^{-1} cm^{-1}) measured under the same conditions. The low conductivity of the compound under consideration is apparently due to the integer charge on the BEDT—TTF molecule (+1) and is typical of other BEDT—TTF radical-cation salts with complete charge transfer.[13]

Therefore, we prepared the first ternary C_{60} complex, *viz.*, $C_{60} \cdot (BEDT—TTF \cdot I_3)$, containing the $BEDT—TTF^{\cdot +}$ radical cation. In this compound, the C_{60} fullerene molecules are neutral. Consequently, the $BEDT—TTF^{\cdot +}$ radical cations are bound to the C_{60} molecules apparently through van der Waals forces.

The proposed procedure for the synthesis of C_{60} complexes using radical-cation salts of tetrathiafulvalenes allows the preparation of ternary C_{60} compounds containing radical cations of tetrathiafulvalenes and counterions. Of prime importance is the fact that these compounds can be prepared as single crystals. High polarizability of the C_{60} molecules can strongly affect the conducting and magnetic properties of these compounds.

Table 1. Binding energies (E_b) and half-widths (Δ) of the analytical XPS lines

Compound	E_b/eV			Δ/eV		Reference
	S2p	$I3d_{5/2}$	C1s	S2p	$I3d_{5/2}$	
$C_{60} \cdot (BEDT—TTF \cdot I_3)$	164.1	619.4	2.1	2.6	2.3	—
$(BEDT—TTF)_2 \cdot I_3$	163.8	619.0	2.0	2.4	2.1	21
BEDT—TTF	163.6	—	1.9	2.4	—	22
$(Ph_4P)_2C_{60} \cdot I$	—	617.7	2.1	—	2.2	23

Experimental

The starting compound $BEDT—TTF \cdot I_x$ ($x \approx 3.4$) was prepared by oxidation of BEDT—TTF (30 mg, 0.077 mmol) in benzonitrile (50 mL) with an excess of I_2 (118 mg, 0.466 mmol) on heating. After cooling of the solution, the finely crystalline precipitate that formed was filtered off, washed with acetone, and dried in air. Found (%): I, 52.3; S, 29.17. $BEDT—TTF \cdot I_{3.4}$. Calculated (%): I, 52.7; S, 31.2.

The $C_{60} \cdot (BEDT—TTF \cdot I_3)$ compound was prepared in quantitative yield by cocrystallization of stoichiometric amounts of $BEDT—TTF \cdot I_{3.4}$ and C_{60} in benzonitrile. The resulting crystals were washed with acetone and dried in air. The compound was obtained as rhombic crystals with dimensions of up to 0.5 mm. Found (%): C, 56.4; H, 0.74; I, 26.20; S, 17.14. $C_{70}H_8I_3S_8$. Calculated (%): C, 56.7; H, 0.53; I, 25.6; S, 17.14.

The IR transmission spectrum of single crystals of $C_{60} \cdot (BEDT—TTF \cdot I_3)$ was measured in the region of 650—

4000 cm^{-1} on a Perkin—Elmer 1760 Fourier-transform IR spectrometer equipped with a microscope and an MST detector.

The electronic reflection spectra of single crystals were measured on a double-beam microspectroreflectometer equipped with a Glan—Thompson prism as the polarizer; the diameter of the probe was 25 μm; the spectral width of the aperture $\Delta\lambda$ = 2 nm. Quartz and SiC crystals were used as the standards. The reflection coefficient was measured using the best reflecting region of the surface.

The samples for X-ray photoelectron spectra were prepared according to a procedure reported previously.[24] The spectra (Mg-Kα radiation, $h\nu$ = 1253.6 eV) were calibrated using the C1s peak (285.0 eV).

The X-ray powder data were obtained on an automated DRON-3 diffractometer (Cu-Kα radiation, λ = 1.5418 Å, graphite monochromator). The measurements were performed in the continuous scanning mode at a rate of 4 deg min^{-1}. The sample was applied to a flat glass holder from a dispersion in heptane. A total of 28 reflections were obtained in the 4—64° range. The initial indexing of the unit cell was carried out using the TREOR program.[25] The obtained parameters were refined using the PIRUM program.[26]

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