

The first complex of C₆₀ fullerene with bis(ethylenedithio)tetrathiafulvalene radical cation: C₆₀ • (BEDT—TTF • I₃)

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The complex of C₆₀ fullerene containing the radical cation of the organic donor, viz., C₆₀ • (BEDT—TTF • I₃), 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, $\beta = 99.00(1)^\circ$. The IR and electronic spectra of single crystals of the complex have absorption bands characteristic of the BEDT—TTF^{•+} radical cation and neutral C₆₀. The ESR spectrum has a signal with $g = 2.0074$ and $\Delta H_{pp} = 23$ G belonging to BEDT—TTF^{•+}. The position of the 13d_{5/2} peak in the X-ray photoelectron spectrum confirms the formation of the I₃[−] anion.

Key words: C₆₀ fullerene; bis(ethylenedithio)tetrathiafulvalene; complexes of radical cations; electronic reflection spectra; XPS, IR, and ESR spectra.

A large number of donor-acceptor complexes with C₆₀ 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 C₆₀. 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 = I₃[−], IBr₂[−], AuI₂[−], ReO₄[−], or Cu(NCS)₂[−]) and (BEDT—TTF)₄Hg_{2.89}Hal₈ (Hal = Cl or Br).¹³

The C₆₀ and C₇₀ fullerenes form neutral complexes with BEDT—TTF. These complexes were prepared by cocrystallization of C₆₀ or C₇₀ and BEDT—TTF from carbon disulfide ((BEDT—TTF)₂C₆₀⁴ and BEDT—TTF • C₇₀ • CS₂⁵), toluene, benzonitrile ((BEDT—TTF)₂C₆₀⁶), or pyridine ((BEDT—TTF)₂C₆₀(Py)₂⁵).

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_kC₆₀(Solv)_x compounds (where D is the donor and Solv is the solvent) with iodine to change the neutral state of molecular C₆₀ 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⁺ • C₆₀ • 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 C₆₀ • (BEDT—TTF • I₃) containing the radical cation (BEDT—TTF^{•+}).

Results and Discussion

The crystals of the C₆₀ • (BEDT—TTF • I₃) 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, $\beta = 99.00(1)^\circ$. 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., C₂, C_m, or C_{2/m}. In these unit cells, each fullerene molecule can have six neighboring C₆₀ molecules located at approximately equal

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 $\pm 0.5 \pm 0.50$) 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

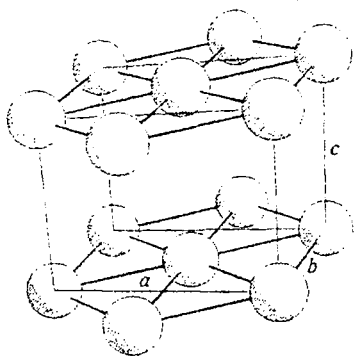


Fig. 1. Scheme of the arrangement of C_{60} molecules in the unit cell of $C_{60} \cdot (BEDT-TTF \cdot I_3)$. The C_{60} molecules are represented by balls. The crystallographic directions and the shortest distances between the centers of the C_{60} molecules are indicated by thin lines.

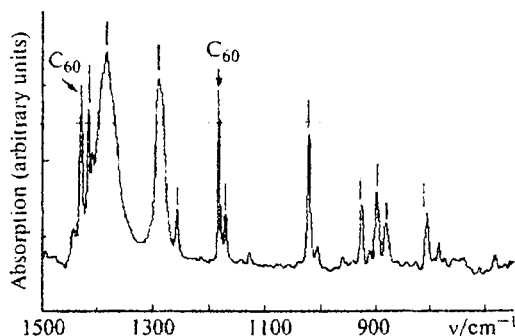


Fig. 2. IR spectrum of single crystals of $C_{60} \cdot (BEDT-TTF \cdot I_3)$. The absorption bands of the $BEDT-TTF^{+\cdot}$ radical cation and C_{60} fullerene are marked.

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}

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 data¹⁶) and of the crystal of the $(BEDT-TTF)_2I_3$ radical-cation salt¹⁷ 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} molecules¹⁹ 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

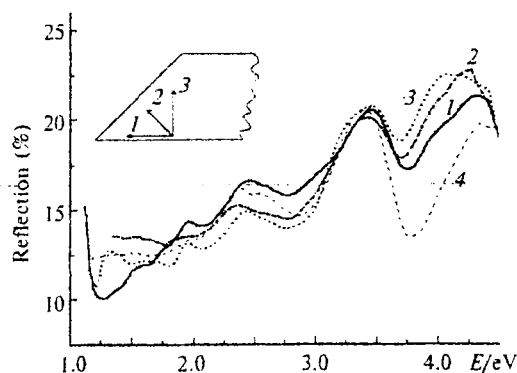


Fig. 3. Electronic reflection spectra of single crystals of $C_{60} \cdot (BEDT-TTF \cdot I_3)$ measured from the developed face in three polarizations (1, 2, and 3) and the reflection spectrum of the crystal of the initial C_{60} (4).

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 *I* (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^- anion¹⁷ 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 $\Delta H_{pp} = 23$ G corresponding to the $BEDT-TTF^{\cdot+}$ radical cation. As the temperature decreases, the position and the width of the signal remain virtually un-

changed ($g = 2.0074$ and $\Delta H_{pp} = 20$ 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 -($BEDT-TTF$)₂ I_3 salt gives the ESR signal with $\Delta H_{pp} = 18$ –24 G (300 K) and $\Delta H_{pp} = 2$ G (5 K) and the θ -($BEDT-TTF$)₂ I_3 salt gives the ESR signal with $\Delta H_{pp} = 60$ –80 G (300 K) and $\Delta H_{pp} = 28$ G (108 K).¹³ The initial $BEDT-TTF \cdot I_{3,4}$ compound is characterized by the ESR signal with $g = 2.0043$ and $\Delta H_{pp} = 25$ G (300 K), whose parameters also change as the temperature decreases ($g = 2.0059$ and $\Delta H = 10$ 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.

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–

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

Compound	E_b /eV			Δ /eV			Ref- erence
	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	21
$BEDT-TTF$	163.6	—	1.9	2.4	—	22	22
$(Ph_4P)_2C_{60} \cdot I$	—	617.7	2.1	—	2.2	23	23

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-K α 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-K α radiation, $\lambda = 1.5418$ 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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