Molecular complex of C_{60} fullerene with an organic π-donor, bis(methylenedithiotetrathiafulvalene): synthesis, crystal structures, and properties

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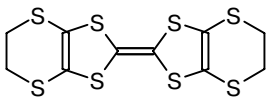
A new molecular complex based on [60]fullerene, namely, (BMDT-TTF) · C_{60} · $2CS_2$ (**1**) (where BMDT-TTF is bis(methylenedithiotetrathiafulvalene)) was synthesized. The molecular and crystal structures of **1** were established by X-ray diffraction analysis. Complex **1** has a layered structure, layers of C_{60} molecules alternating with those formed by BMDT-TTF molecules and CS_2 molecules located between them. In complex **1**, there are short contacts between C_{60} and the donor molecules, which results in a changed BMDT-TTF geometry. The donor molecules in **1** form in addition short S...S contacts. The data of IR spectroscopy indicate that the charge transfer to the fullerene molecule is insignificant if at all present. The conductivity of a single crystal of **1** measured at ~20 °C using a four-contact method is $2 \cdot 10^{-5}$ $(\Omega\ cm)^{-1}$.

Key words: C_{60} fullerene, molecular complexes, synthesis, X-ray diffraction, crystal structure, intermolecular interactions, IR spectroscopy, electrical conductivity.

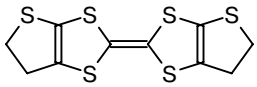
The C_{60} fullerene and its derivatives represent a new type of materials with physicochemical characteristics attractive from both the fundamental and applied standpoints. The enhanced interest in the compounds based on fullerene is due to the recent discovery of superconductivity[1,2] and ferromagnetism[3] for them. The C_{60} fullerene exhibits electron-acceptor properties and forms molecular charge transfer complexes (CTC) with organic donor molecules based on tetrachalcogenafulvalenes. Many of these donors form radical cation salts that possess electrical conductivity and magnetic properties.[4] Previously, molecular complexes of C_{60} with symmetric and asymmetric tetrachalcogenafulvalenes, namely, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF),[5—7] bis(ethylenethio)tetrathiafulvalene (BET-TTF),[8] tetramethyltetraselenafulvalene (TMTSF),[9—11] bis(ethylenedithio)tetraselenafulvalene (BEDT-TSF),[12] and 2-(4-thiono-1,3-dithiolan-5-ylidene)-4,5-dimethyl-1,3-diselenol (DTDS)[13] have been prepared and investigated.

It was found that the formation of CTC by C_{60} fullerene is largely determined by the ability of the donor molecule to change its geometry to fit the fullerene spherical shape.

This work is devoted to the synthesis of novel CTC (BMDT-TTF) · C_{60} · $2CS_2$ (**1**) and to the study of its crystal structure, IR spectra, and the electrical conductivity of single crystals (where BMDT-TTF is bis(methylenedithiotetrathiafulvalene)).



BEDT-TTF



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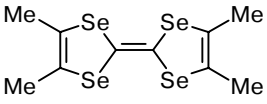
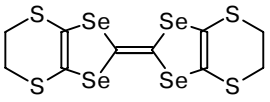
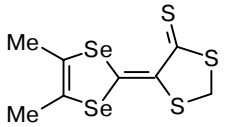


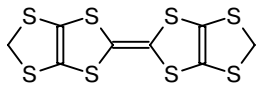
TMTSF



BEDT-TSF



DTDS



BMDT-TTF

Experimental

IR spectra were measured on a Specord IR-75 spectrophotometer in KBr pellets at ~20 °C. Conductivity measurements

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for single crystals of **1** were carried out using a four-contact method at a constant current and ~20 °C. The crystals were glued to a platinum wire of diameter 10 μ using a graphite paste. The conductivity of single crystals of **1** was $2 \cdot 10^{-5}$ $(\Omega\ cm)^{-1}$, which is a normal value for fullerene-based CTC.

Fullerene C_{60} was 99.98% pure according to HPLC. The material was synthesized at the Rasuvaev Institute of Organonmetallic chemistry of the RAS. CS_2 (Aldrich) was used as a solvent.

Synthesis of complex 1 single crystals. Single crystals of **1** were prepared from a CS_2 solution containing 1.5 mmol of BMDT-TTF and 0.6 mmol of C_{60}. The red solution was kept for 30 min at 50 °C under argon and then slowly cooled at a rate of 1 K h^{-1}. The solvent was slowly evaporated at ~20 °C over a period of 5 days until its volume was 3 ml. This gave shiny black-colored crystals shaped like enongated prisms. The crystals were filtered off, washed with anhydrous EtOH, and dried *in vacuo*. The stoichiometry of the complex (BMDT-TTF) · C_{60} · $2CS_2$ (**1**) was determined using elemental analysis and confirmed by an X-ray diffraction study. Found (%): C, 69.12; H, 0.30; S, 30.83. $C_{70}H_4S_{12}$. Calculated (%): C, 68.40; H, 0.30; S, 31.30.

X-ray diffraction study of complex 1 was carried out using a KM-4 KUMA Diffraction four-circle automated diffractometer (ω/2θ scan mode, CuKα radiation, graphite monochromator). Crystals of (BMDT-TTF) · C_{60} · $2CS_2$ (**1**): $C_{70}H_4S_{12}$, M = 1229.45, monoclinic, a = 13.550(5) Å, b = 9.964(7) Å, c = 17.125(8) Å, β = 99.52(4)°, V = 2280(2) $Å^3$ (the parameters were refined by the least-squares method over 25 strong, automatically centered reflections, α = 1.5418 Å), space group $P2_1/m$, Z = 2, d_{calc} = 1.791 mg m^{-3}, $F(000)$ = 1232, sample dimensions 0.32 × 0.25 × 0.20 mm; T_{exp} = 300 K. The number of measured reflections was 4720 (4574 independent reflections), $(2\theta)_{max}$ = 160.64°, range of measurements h,k,l: $-17 \le h \le 17$, $0 \le k \le 12$, $0 \le l \le 19$. The absorption correction was not applied (μ (Cu-Kα) = 5.783 mm^{-1}).

The crystal structure of **1** was solved by the direct method using the SIR92 program package[14] and refined by the least-squares method in the anisotropic approximation using the SHELXL-93 program package.[15] The hydrogen atoms were not located. The final R factor was 0.10 for 1309 reflections with $I > 2\sigma(I)$. The relatively high R factor can be explained by the disorder of C_{60} molecules in the crystal. This is confirmed by high values of equivalent isotropic parameters for the thermal displacements of fullerene C atoms and also by the presence of additional electron density peaks near the main positions of these atoms in the Fourier difference synthesis. When the additional positions of C atoms are included in the refinement with different populations, the R factor decreases to 0.07. The bond lengths in the fullerene cage were fixed in the refinement because of the limited set of experimental data available. All calculations were performed using a Pentium 100 PC and the WinGX program package.[16]

Results and Discussion

Complex **1** has a layered crystal structure. The layers of fullerene molecules are separated by layers of BMDT-TTF donor molecules (Fig. 1). The CS_2 molecules are located between the BMDT-TTF molecules. In complex **1**, the m-plane passes through the centers of fullerene molecules and along the central C=C bonds of BMDT-TTF. Two independent CS_2 molecules are located in the m-plane.

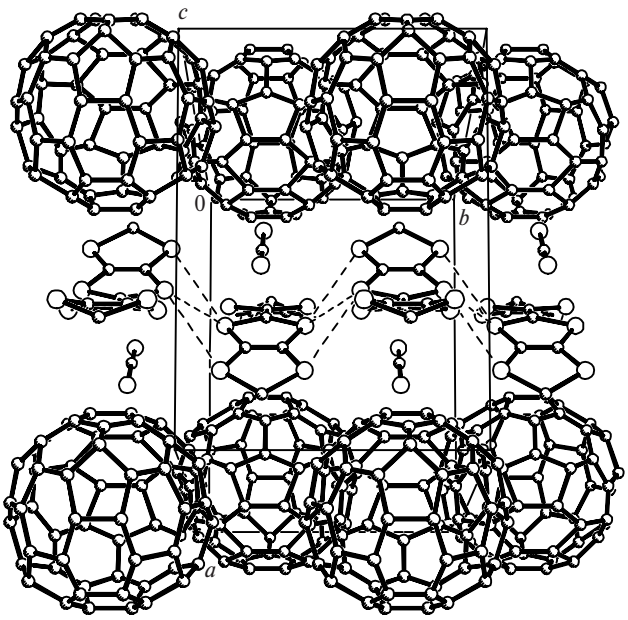

Fig. 1. Crystal structure of the (BMDT-TTF) · C_{60} · $2CS_2$ complex (fragment).

Neighboring BMDT-TTF molecules in the layers form short S...S contacts of the "side-by-side" type (S(1)—S(1′): $(-x + 1, -y + 1, -z + 1)$, 3.283(3) Å and S(1)—S(2′): $(-x + 1, -y + 1, -z + 1)$, 3.519(3) Å). The shortened intermolecular S...S contacts (the normal contact value is 3.68 Å[17]) are similar to those observed in the structures of molecular conductors.[4] The existence of such layers, which are discovered for the first time in a [60]fullerene CTC, suggests that conductive compounds might be developed on the basis of this complex.

The BMDT-TTF molecule in structure **1** occurs in a nonplanar conformation (Fig. 2) due to the shortened S...C and C...C* intermolecular contacts between fullerene and the BMDT-TTF molecules (S(2)—C(16): $(-x + 1, -y + 1, -z + 1)$, 3.47(2) Å; C(2)—C(32): $(x + 1, y, z)$, 3.34(2) Å; C(2)—C(32): $(x + 1, -y + 1/2, z)$, 3.35(2) Å). The C(6) atom in the BMDT-TTF molecule is deflected in the direction opposite to the bend of BMDT-TTF. Thus, upon complex formation, the donor molecule acquires a new conformation in which the closest distance to fullerene is attained.

The frequencies of the absorption maxima in the IR spectra of BMDT-TTF, complex **1**, and neat C_{60} measured in KBr pallets are given in Table 1. The spectrum of the complex has strong bands at 526, 577, 1182, and 1428 cm^{-1}, which correspond to C_{60} and virtually do not differ in positions from the bands observed for free C_{60}. The bands due to BMDT-TTF incorporated in complex **1** are shifted with respect to those for pure

* The standard contact values are 3.55 and 3.42 Å, respectively.

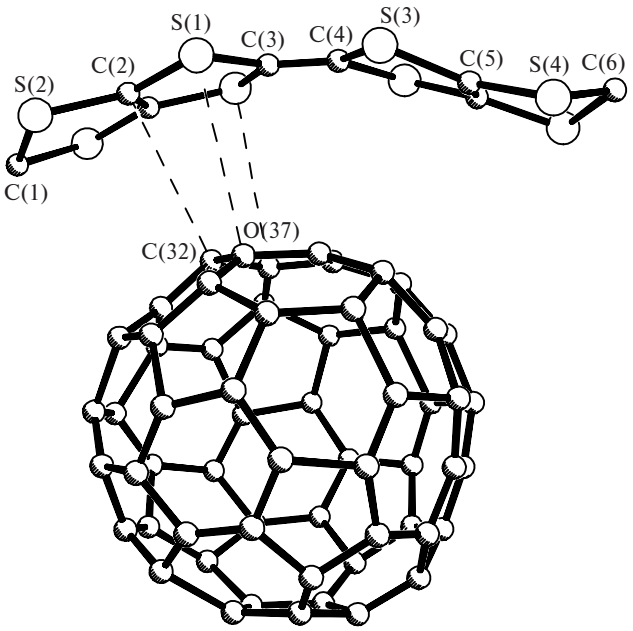

Fig. 2. Fragments of C_{60} and BMDT-TTF molecules involved in C...C nonvalence interactions.

Table 1. Vibration frequencies (ν/cm^{-1}) in the IR spectra of BMDT-TTF and C_{60} molecules and the (BMDT-TTF) · C_{60} · CS_2 complex

BMDT-TTF	C_{60}	(BMDT-TTF) · C_{60} · $2CS_2$
408	—	408
484	—	483
—	526	526
—	577	577
684	—	684
707	—	707
760	—	760
847	—	847
963	—	963
1096	—	1096
—	1182	1182
—	1428	1428
—	—	1510

BMDT-TTF by no more than 1 cm^{-1}, which is within the error of measurements. Additionally, the spectrum of complex **1** exhibits a band at 1510 cm^{-1} corresponding to the CS_2 molecule. On the whole, the IR spectra point to the formation of a weak CTC of BMDT-TTF with C_{60}[18].

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