

Charge Transfer Complexes of C_{60} and C_{70} with 9,9'-Trans-Bis (Telluraxantenyl)

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New molecular complexes of fullerene C_{60} and C_{70} with 9,9'-trans-bis (telluraxantenyl): $BTX \cdot C_{60} \cdot CS_2$, $BTX \cdot C_{60}$ and $BTX_{1.25} \cdot C_{70} \cdot (CS_2)_{1.30}$ were synthesized. IR-, XPS-, EPR-spectra were studied, the crystal structure of $BTX \cdot C_{60} \cdot CS_2$ complex was determined.

The discovery of superconductivity of the compounds of fullerene with alkali metals¹ and ferromagnetism in the salts of C_{60} with strong donor TDAE² evoked a great interest to the synthesis of ion-radical salts and charge transfer complexes of fullerene with organic and metalorganic donors. Till now, a series of the compounds of fullerenes with organic donors of different classes was obtained.³⁻⁶ The specific feature of the donors interacting with C_{60} , was a steric ability of a molecule to conformational changes and the availability of aromatic substituents and heteroatoms. The utilization of different types of donors gave a wide opportunity for the synthesis of the compounds with various C_{60} packings in a crystal, thus stipulating the differences in the properties of the compounds obtained. However, the structural peculiarity of C_{60} molecule and the instability of its compounds in the anion-radical state made the problem of obtaining fullerene compounds as stable single crystals very actual.

In this work we report on the synthesis of new charge transfer complexes of C_{60} and C_{70} with organic Te-containing donor 9,9'-trans-bis(telluraxantenyl) (BTX): $BTX \cdot C_{60} \cdot CS_2$, $BTX \cdot C_{60}$ and $(BTX)_{1.25} \cdot C_{70}(CS_2)_{1.30}$, the preparation of $BTX \cdot C_{60} \cdot CS_2$ single crystals and some properties of these compounds.

BTX molecule (Figure 1) consists of two nonplanar tellura-xantene fragments, which have a conformation of a "butterfly", they are in a trans position to one another and are connected by the inversion center.⁷ The structure of BTX molecule in tetracyano-quinodimethane $BTX \cdot TCNQ^8$ complex is analogous.

$BTX \cdot C_{60} \cdot CS_2$ (1) was obtained by the evaporation of the solutions of C_{60} and BTX in carbon disulfide at 1:1 molar ratio during a week. (1) was crystallized as well-formed planar parallelepipeds of black color with dark-red translucency. Elemental analysis yielded $C_{87}H_{18}Te_2S_2$. Found %: C = 75.60; H = 1.73; S = 4.45. Calculated %: C = 75.50; H = 1.30; S = 4.63; Te = 18.48.

$BTX \cdot C_{60}$ (2) was obtained by mixing the hot equimolar solutions of C_{60} in toluene and BTX in 1,2-dichloroethane with the following evaporation during 3 hours. Elemental analysis yielded $C_{86}H_{18}Te_2$. Found %: C = 79.15; H = 2.01. Calculated %: C = 79.07; H = 1.38; Te = 19.55. The compound (2) appears as black plates with red-brown translucency.

$(BTX)_{1.25}C_{70}(CS_2)_{1.30}$ (3) was obtained by the evaporation of equimolar solution of C_{70} and BTX in carbon disulfide during a week. Elemental analysis yielded $BTX_{1.25}(C_{70})(CS_2)_{1.30}$. Found %: C = 75.60; H = 2.14; S = 5.22. Calculated %: C = 74.80; H = 1.34; S = 4.78; Te = 19.08.

The crystals of all complexes were washed with ether and dried in air. The yield of the compounds was quantitative.

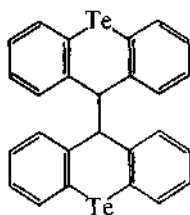


Figure 1 The donor 9,9'-trans-bis(telluraxanteny) (BTX).

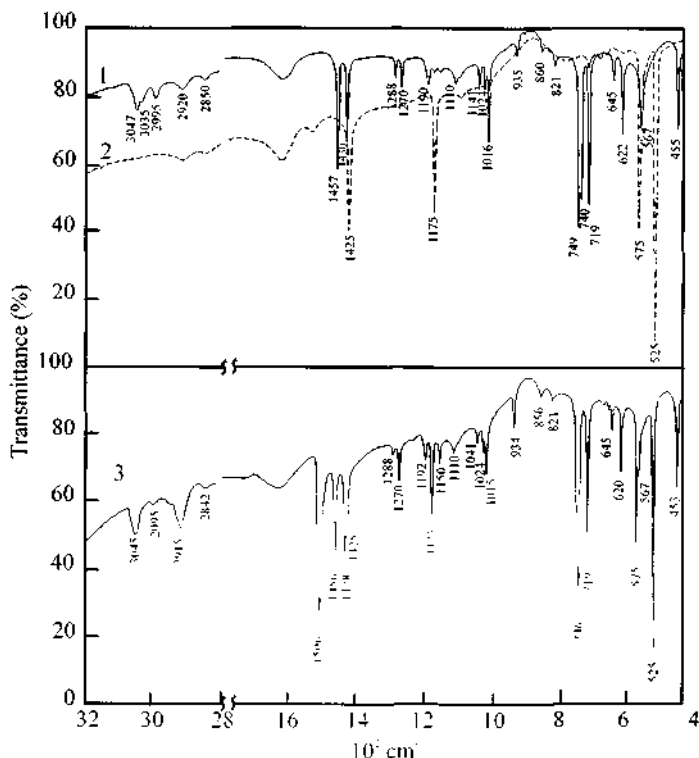


Figure 2 IR-spectra of BTX (1), C_{60} (2) and of the complex $BTX \cdot C_{60} \cdot CS_2$ (3) (tablet in KBr, Specord 75 IR).

The compounds obtained were characterized by IR absorption spectra (Figure 2), which were registered by using "Specord 75 IR" spectrophotometer. The error in the wave number was $\pm 1 \text{ cm}^{-1}$. The samples were prepared as tablets in KBr. IR-spectra of the complexes contain a full set of the absorption bands of the components of the complex. The absorption band at 1508 cm^{-1} in the spectra of complexes (1) and (3) corresponds to ν_{CS_2} in CS_2 . The frequencies and the intensity ratio of adsorption band of the fullerenes in the spectra of the complexes remain unchanged as compared to those of the individual fullerenes, except the intensities of some oscillations of C_{70} in complex (3)

which increased up to 10 % - 20 %. Some absorption bands of the donor were shifted by 2 cm⁻¹ to 7 cm⁻¹ to a low-frequency range with the simultaneous redistribution of the intensity of the absorption bands: the intensity of absorption bands at 1270 cm⁻¹, 1015 cm⁻¹, 620 cm⁻¹, 453 cm⁻¹ decreased down to 25 % for all complexes, the intensity of absorption bands at 3045 cm⁻¹, 1456 cm⁻¹, 1428 cm⁻¹ increased up to 25 % for complexes (1) and (2) and the intensity of σ_{CH} at 746 cm⁻¹ increased 1.5 times (2 times for (3)) due to the formation of fullerenes complex with BTX. The change in the intensities of the absorption bands of the donor was caused by the changes of the dipole moments of CH bonds in BTX because of π - π interaction of the unsaturated bonds of fullerenes and BTX aromatic rings.

The study of the thermal stability of the compounds (1) and (2) was carried out. Thermogravimetric analysis was made under argon by using "Thermograph Q" calorimeter, in 298 K to 973 K temperature range. TG and DTG curves showed that (1) lost 5.5 % of its mass in 473 K to 505 K temperature range, corresponded to the removal of carbon disulfide. A partial decomposition of BTX occurred in 613 K - 653 K temperature range in both complexes and was accompanied by the loss of 10 % of the mass for (1) and 11 % of that for (2). It should be noted, that the individual BTX donor began to decompose near 573 K, whereas the temperature of its decomposition in a complex is essentially higher.

The study of X-ray photoelectron (XP) spectra of (1) and (3) was carried out. The spectra were excited by the Mg-K α radiation ($h\nu = 1253.6$ eV). The calibration of the spectra was carried out against the peak C(1s), $h\nu = 285.1$ eV. The binding energy which corresponded to the peak Te(3d_{5/2}) was equal to 574.1 eV \pm 0.2 eV for both complexes but it was equal to 573 eV \pm 0.1 eV for pure BTX. The [C/Te]_{at} ratio, calculated from the integral intensity C(1s) and Te(3d) was equal to 45 for complex (1), which corresponded to the complex of 1:1 composition and it was equal to 41 for complex (3), which corresponded to C₇₀:BTX ratio = 1:1.25 in the complex. The energy of the basic plasmon in the compound (1) was determined from the loss spectra accompanying the photoelectron peak C(1s). The energy 25.2 eV \pm 0.3 eV was less than that of ($\sigma + \pi$) plasmon in fullerite (26.2 eV),⁹ measured by the same method. It is interesting that the shoulder from the side of higher energy of the bond from basic peaks appeared in XP spectrum of the complex (3) on the peak Te(3d) which corresponded to Te⁺⁴. This shoulder is absent in the complex with C₆₀.

X-ray study of crystals of (1) was carried out. The basic X-ray data are the following: $a = 10.309$ (1) Å, $b = 10.988$ (3) Å, $c = 12.011$ (1) Å, $\alpha = 85.20(2)^\circ$, $\beta = 71.85(1)^\circ$, $\gamma = 79.83(2)^\circ$, $V = 1272$ Å³, Space group P $\bar{1}$, $Z = 1$. The intensities of 3908 independent reflexes with $I > 3\sigma$ (1) were measured with Enraf-Nonius CAD4 automatic diffractometer on Mo-K α radiation. The structure was determined by a direct method. It was found that C₆₀, CS₂ and BTX molecules are located in the centers of symmetry. At present a more accurate definition of the structure is being carried out by the method of least squares.

It is shown for complexes in the solid state (tablets in KBr) and in solutions, for C₆₀ or C₇₀ and BTX at 1 : 1 molar ratio, that there is no absorption band associated with charge transfer in the near IR range. EPR signal characteristic of C₆₀ anion radical, was not observed for compounds (1) and (2). The conductivity of single crystals of (1) and (3) is less than 10⁻⁷ S · cm⁻¹.

Thus, it is derived from the elemental and thermogravimetric analyses, IR- and UV-spectroscopy that molecular complexes of BTX with fullerene of 1 : 1 composition were obtained. If the reaction was carried out in carbon disulfide, then one molecule of CS₂ is involved in BTX · C₆₀ · CS₂ complex. The presence of the shoulder on the peak Te(3d) in BTX complex with C₇₀ attributed to Te⁺⁴, the ratio C₇₀:BTX = 1:1.25 calculated from XP-spectra and the data of elemental analysis stipulate a noninteger composition of the complex: BTX_{1.25}C₇₀(CS₂)_{1.30}. At present the real reason of the appearing of Te⁺⁴ has not been determined.

Thus, molecular complexes of C₆₀ and C₇₀ were obtained with a new type of donor of xantylene class. The interaction seems to be realized between 3d electrons of Te atom and π -systems of phenyl

rings of BTX and fullerenes. The bulky configuration of donor molecule, which consists of two symmetrical nonplanar fragments, facilitates the interaction. The preparation of stable single crystals enables one to study their physical properties and the doping of these compounds.

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