Molecular complexes of fullerene with 9,9′-*trans*-bis(telluraxanthenyl) (BTX): BTX·C_{60}·CS_2 and BTX·C_{60}

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New molecular complexes of fullerene with 9,9′-*trans*-bis(telluraxanthenyl) **(BTX): BTX·C_{60}·CS_2 and BTX·C_{60} have been synthesized; single crystals of these compounds have been obtained and their IR, XPS and EPR spectra studied.**

The discovery of the superconductivity of compounds of fullerene with alkali metals[1,2] and ferromagnetism in the salts of C_{60} with strong donor tetrakis(dimethylamino)ethylene[3] has evoked considerable interest in the synthesis of ion-radical salts and charge-transfer complexes of fullerene with organic and metallorganic donors. Until now, only the series of compounds of fullerene with organic donors of different classes has been obtained: $Fe(C_5H_5)(C_6Me_6)$,[4] ferrocene $[(C_5H_5)_2Fe]_2{\cdot}C_{60}$,[5] hexamethoxytriphenylene $(HMT)_2{\cdot}C_{60}$,[6] sulfur- and tellurium-containing derivatives of tetrathiafulvalene: bis(ethylenedithia)tetra-thiafulvalene (BEDT–TTF)$_2$·C_{60},[7] bis(dimethylthieno)tetratellurafulvalene (BDMT–TTeF)·C_{60}·CS_2[8] and some others. A specific feature of the donors interacting with C_{60} is the steric ability of a molecule to undergo conformational changes and the availability of aromatic substituents and heteroatoms. The utilization of different types of donors provides a wide opportunity for the synthesis of compounds with various C_{60} packings in the crystal, thus defining differences in the properties of the compounds obtained. However, the structural peculiarity of C_{60} and the instability of its compounds in the anion-radical state has made the problem of obtaining fullerene compounds as stable single crystals very acute.

In this work we report on the synthesis of new charge transfer complexes of C_{60} with organic tellurium-containing donor 9,9′-*trans*-bis(telluraxanthenyl) (BTX): BTX·C_{60}·CS_2 and BTX·C_{60}, the preparation of BTX·C_{60}·CS_2 single crystals and some properties of these compounds.

BTX (Figure 1) consists of two non-planar telluraxanthene fragments in a 'butterfly' conformation. They are in a *trans* position to one another and are connected by an inverse centre.[9] The structure of BTX in the tetracyanoquinodimethane BTX·TCNQ[10] complex is analogous.

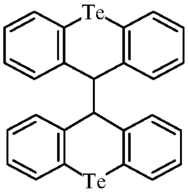

Figure 1 The donor 9,9′-*trans*-bis(telluraxanthenyl).

BTX·C_{60}·CS_2 **1** was obtained by the evaporation of solutions of C_{60} and BTX in carbon disulfide (1:1 molar ratio) during a week. Compound **1** was crystallized as well-formed black planar parallelepipeds of dark-red translucency. Crystals of the highest quality were obtained by evaporation of a saturated solution. The crystals were washed with ether and dried in air. The yield of the compounds was quantitative. Elemental analysis yielded $C_{87}H_{18}Te_2S_2$. Found: C 75.60; H 1.73; S 4.45. Calc.: C 75.50; H 1.30; S 4.63; Te 18.48 %.

BTX·C_{60} **2** was obtained by mixing hot equimolar solutions of C_{60} in toluene and BTX in 1,2-dichloroethane with subsequent evaporation during 3 h. The remaining solvent was decanted from the crystals precipitated. The crystals of **2** were washed with ether, yield 90%. Elemental analysis yielded $C_{86}H_{18}Te_2$. Found: C 79.15; H 2.01. Calc.: C 79.07; H 1.38; Te 19.55 %. Compound **2** appears as black plates of red-brown translucency.

A study of the thermal stability of the compounds obtained was carried out. Thermogravimetric analysis was performed under argon by using a 'Thermograph Q' calorimeter in the 298–973 K temperature range. TG and DTG curves showed that **1** lost 5.5% of its mass in the 473–505 K temperature range, which corresponded to the removal of carbon disulfide from the complex. This is confirmed by the elemental analysis data. That such a high temperature is required for the elimination of CS_2 (bp 46 °C) indicates its strong binding in the complex. Partial decomposition of BTX occured in the 613–653 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**. According to IR spectra the residues of the complexes **1** and **2** contained absorption bands attributed to the individual C_{60} molecule against a background of wide absorption bands, probably associated with the presence of carbon remaining after BTX decomposition. 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 significantly higher.

The compounds obtained were characterized by IR absorption spectra (Figure 2), which were recorded using a 'Specord 75 IR' spectrophotometer. The error in the wavenumber was $\pm 1\,\text{cm}^{-1}$ and the error in y-coordinate was ±1 %. The samples were prepared as tablets in KBr. The IR spectrum of complex **1** contains a full set of the absorption bands of the components of the complex. Absorption bands at 1425, 1175, 575 and 525 cm^{-1} correspond to oscillation modes of C_{60}. Their frequencies and the intensity ratio remain unchanged as compared with the individual C_{60} molecule. The absorption band at 1508 cm^{-1} corresponds to ν_{cs} in CS_2. BTX donor was indicated in the spectrum of the complex by the following absorption bands: 3045 (ν_{CH}), 1456 and 1428 cm^{-1}(ν_{CC}), 1270 and 1015 cm^{-1} (δ_{CCH} in-plane), 746 and 719 cm^{-1} (δ_{CH} out-of-plane), 620 and 453 cm^{-1} (δ_{CC} skeletal) of the *ortho*-substituted ring. The IR spectrum of complex **2** is completely identical to the absorption band of complex **1** except for the absence of the absorption band at 1508 cm^{-1} corresponding to CS_2. Some absorption bands of the donor were shifted to a low-frequency range by 2 cm^{-1} with simultaneous redistribution of the intensity of the absorption bands: the intensity of bands δ_{CCH} and δ_{CC} decreased down to 25 %, the intensity of bands ν_{CH} and ν_{CC} increased up to 25% and the intensity of δ_{CH} at 746 cm^{-1} increased 1.5 times due to the formation of a C_{60} complex with the donor. The change in the intensities of the absorption bands of the donor was caused by changes in the dipole moments of CH bonds in

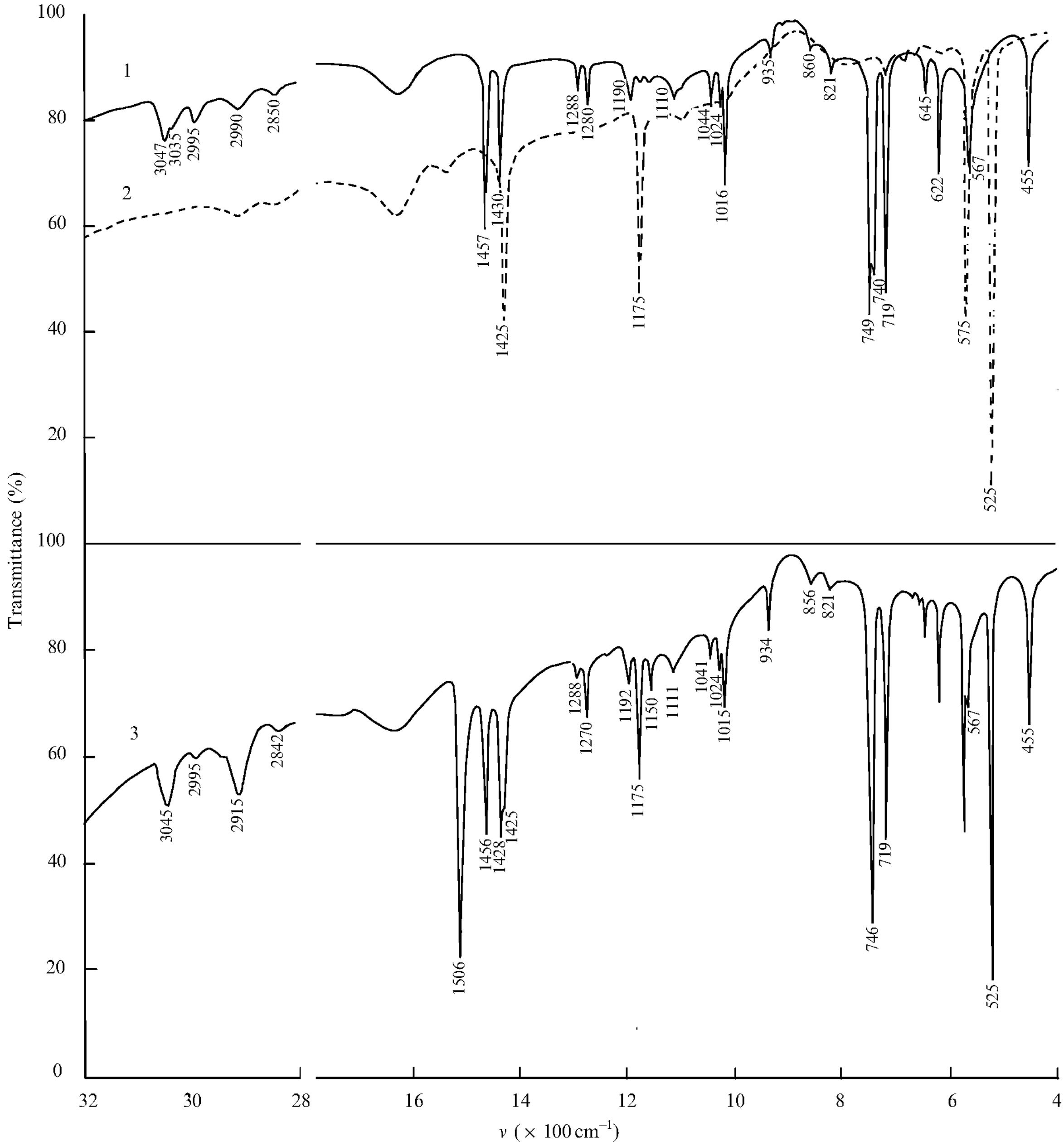

Figure 2 IR spectra of BTX (1), C_{60} (2) and of the complex BTX·C_{60}·CS_2 (3) (tablet in KBr, Specord 75 IR).

BTX·C_{60} because of π–π interaction between the unsaturated bonds of C_{60} and the BTX aromatic rings.

A study of the XPS spectra of **1** was carried out. The spectra were excited by the radiation Mg-K_α ($h\nu$ = 1253.6 eV). The calibration of the spectra was carried out against peak C 1s (285.1 eV). Quite intensive peaks associated with the presence of tellurium in the donor molecule were observed in the XPS of the complex **1** besides the peak C 1s. The binding energy which corresponded to the peak Te 3d$_{5/2}$ was equal to 574.1 ± 0.2 eV, close to the binding in Ph_2Te_2.[11] The [C/Te]$_{at}$ ratio, calculated from the integral intensity C 1s and Te 3d was equal to 45, corresponding to a complex of 1:1 composition. The energy of the basic plasmon in compound **1** was determined from the loss spectra accompanying the photoelectron peak C 1s. This energy was less than that of the $(\sigma + \pi)$ plasmon in fullerite, measured by the same method.[12]

An X-ray study of crystals of **1** was carried out. Basic X-ray data are: $a = 10.309(1)$, $b = 10.988(3)$, $c = 12.011(1)$ A, $\alpha = 85.20(2)°$, $\beta = 71.85(1)°$, $\gamma = 79.83(2)°$, $V = 1272$ A^3, Space group $P\bar{1}$, $Z = 1$. The intensities of 3908 independent reflections with $I > 3\sigma$ were measured with an Enraf-Nonius CAD4 automated diffractometer using Mo-K_α radiation. The structure was determined by a direct method and was refined by a least-squares method with $R = 0.057$. It was found that C_{60}, CS_2 and BTX molecules are located at the centres of symmetry. The complete structure of BTX·C_{60}·CS_2 together with its physical properties will be published soon.

It is shown for **1** and **2** both, in the solid state (tablets in KBr) and in solutions of C_{60} and BTX (1:1 molar ratio), that there is no absorption band associated with charge transfer in the near IR range. An EPR signal characteristic of the $C_{60}^{\cdot -}$ anion radical was not observed for both compounds. The conductivity of single crystals of **1** is less than 10^{-7} S cm^{-1}.

Thus, we conclude from elemental and thermogravimetric analyses and IR and XPS spectroscopy that molecular complexes of BTX with fullerene of 1:1 composition were obtained. If the reaction is carried out in carbon disulfide then one molecule of CS_2 is involved in the BTX·C_{60}·CS_2 complex.

The conductivity and EPR and IR spectroscopic data indicate that the compounds obtained are complexes formed by a weak charge-transfer from BTX to C_{60}.

Thus, molecular complexes of C_{60} were obtained with a new type of xanthene donor. Interaction seems to be achieved between the 3d electrons of the Te atom and the π-systems of the phenyl rings of BTX and C_{60}. The bulky configuration of the donor molecule, which consists of two symmetrical non-planar fragments, facilitates interaction. The preparation of stable single crystals enables a study of their physical properties and the process of doping of these compounds to be performed.

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