

Core Level X-Ray Photoelectron Spectroscopy Study of a Series of Crystalline Fullerene-Organic Donor Compounds

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X-ray photoelectron spectroscopy was used for the investigation of the states and ratios of elements on the surface of BTX $C_{60}CS_2$, BTX $C_{70}CS_2$, (EDT-TTF) $_2 C_{60}CS_2$, (EDT-TTF) $C_{60}C_6H_6$, (EDY-BEDT-DT) $C_{60}C_6H_6$, (TMDTDM-TTF) $_2 C_{60}(CS_2)_3$, (BEDO-TTF) $_2 C_{60}$, (4TM) $_2 C_{60}C_7H_8$, and (BNDY) (C_{60}) crystals. It was established that the CS_2 molecules are easily desorbed from the subsurface layers of BTX $C_{60}CS_2$, BTX $C_{70}CS_2$, (EDT-TTF) $_2 C_{60}CS_2$ and (TMDTDM-TTF) $_2 C_{60}(CS_2)_3$ crystals under the experimental conditions; the donor/fullerene ratio on the surface differs from that in the bulk in some cases; different oxidation states of donor heteroatoms are observed on the surface of BTX $C_{70}CS_2$ and (BNDY) (C_{60}) crystals.

Introduction

Fullerene compounds have been more and more actively investigated in the last several years. The interest to these objects is caused by a unique molecular structure of fullerenes and solid-state properties of materials on their basis, such as superconductivity of A_3C_{60} , where A is alkali metal, and ferromagnetism of TDAE- C_{60} , where TDAE is tetrakis(dimethylamino)ethylene (see, for example, Refs.[1-3]). Therefore, quite urgent are the studies of the surface of fullerene-based materials, since the state of the surface frequently determines the physical and chemical properties of a material.

In the present paper we report the results of the study of the surface of crystals of some compounds with the general formula $(D)_x F(R)_y$, where F is fullerene C_{60} or C_{70} , D is an organic donor, R is a solvent, $x = 1$ or 2 , $y = 0, 1$ or 3 , by the X-ray photoelectron spectroscopy which permits one to obtain information on the state and the ratio of elements in a subsurface layer (0.4-4

nm) of a solid [4]. Some information on the peculiarities of synthesis, chemical structure and some properties of the materials under study were published earlier [5-10]. For some compounds (BTX C_{60} CS_2 [5,6] and (TMDTDM-TTF) $_2$ C_{60} (CS_2) $_3$ [7]) it was possible to prepare crystals of high enough quality and to carry out the X-ray structural analysis.

Experimental

The complexes of fullerenes C_{60} or C_{70} with organic donors were obtained by the evaporation of mixed solutions of fullerene and donor in CS_2 , benzene or toluene. The following donor molecules were used: 9,9'-trans-bis(telluraxanthenyl) (BTX); ethylenedithiotetrathiafulvalene (EDT-TTF); dibenzotetrathiafulvalene (DB-TTF); 2,2'-ethanediylidenebis(4,5-ethylenedithio-1,3-dithiol) (EDY-BEDT-DT), tetramethylenedithiodimethyltetrathiafulvalene (TMDTDM-TTF), bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF), 4, 5, 11, 12 - tetramethoxythianthrene (4MT), and binaphto[1,6-d,e]-1,3-dithiene-2-ylidene (BNDY). The resulting crystals were washed by ethyl alcohol or ether and characterized by elemental analysis, IR and UV spectroscopies.

X-ray photoelectron spectra (XPS) were excited by Mg-K α -radiation ($h\nu = 1253.6$ eV). Preparation of the samples for XPS spectra is in detail described in [11]. The spectra were calibrated to the C1s peak (285.0 eV). This value corresponds to the position of the C1s peak for pure C_{60} and coincides with the data for C_{60} films deposited on different supports [12]. It is obvious that for weak charge transfer complexes in which a part of carbon atoms of fullerene is much higher than that of the donor, this value is close to 285.0 eV. The transition from the measured integral intensities in XPS spectra to atomic concentrations was realized by using the Scofield data on photoelectron cross-sections of absorption of Mg-K α radiation [13].

Results

The presence of sulphur in BTX C_{60} CS_2 and BTX C_{70} CS_2 crystals was established by using the elemental analysis. The IR spectrum of BTX C_{60} CS_2 exhibits an intensive band at 1508 cm^{-1} , which corresponds to ν_{CS} in CS_2 [5].

Nevertheless the XPS spectrum of BTX C_{60} CS_2 did not exhibit the peaks of sulphur. A similar effect was earlier observed for (TPDP) $(C_{60})_2$ (CS_2) $_{1/2}$ complex [14] where TPDP-2,2',6,6' is tetraphenyldipyranlydene. The Te3d $_{5/2}$ peak in the spectrum of BTX C_{60} CS_2 is shifted by 0.4 eV with respect to that in pure BTX (Fig.1). The Te3d spectra of all investigated BTX C_{70} CS_2 crystals contain the additional peaks shifted by ~ 2 eV to higher energies from the Te $^{2+}$

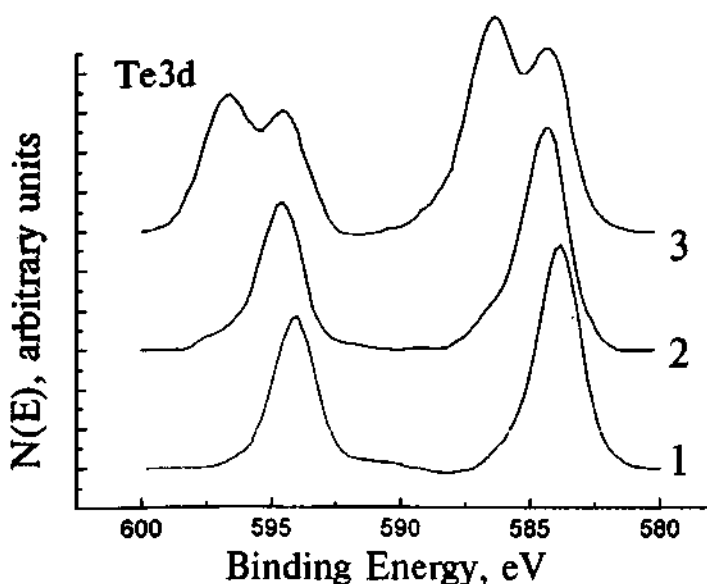


Figure 1. X-ray Te3d photoelectron spectra of BTX (1), BTX C₆₀ CS₂ (2), and BTX C₇₀ CS₂ (3) crystals after the subtraction of a linear background and the normalization to peak intensity.

peaks. Positions of the additional peaks correspond to Te⁴⁺. Nevertheless the IR spectra do not provide any information on the change of the donor conformation in BTX C₇₀ CS₂ crystals as compared with the BTX C₆₀ CS₂ ones.

The C₆₀ complex with EDT-TTF was obtained either from CS₂ or from C₆H₆. For both complexes the shift of the S2p line relative to that of the pure donor was practically equal to zero. The complexes also practically did not differ in the parameters $\Delta S2p$ and ΔCls . However, the [S/C] ratio on the surface of the crystals isolated from different solvents differ by almost a factor of three (see the Table), being in both cases lower than the bulk ratio calculated from the data of the elemental analysis. An essential depletion of the surface of (EDT-TTF) C₆₀ C₆H₆ crystals by the donor was confirmed by repeated syntheses of this compound. A similar, but not well pronounced depletion of the surface by the donor was observed for (DB-TTF) C₆₀ C₆H₆, (BEDO-TTF)₂ C₆₀, and (EDY-BEDT-DT) C₆₀ C₆H₆ crystals (see the Table). It should be noted here that the desorption of such a solvent as benzene from the zone of the analysis should result in the increase in the measured [S/C] ratio.

For (TMDTDM-TTF)₂ C₆₀ (CS₂)₃ crystals whose composition is confirmed by structural studies [7], the [S/C] ratio determined from the XPS spectra is equal to 0.094. The stoichiometric [S/C] ratio is equal to 0.217. Calculation

	Compound	S2p, eV	S2p, eV	C1s, eV	$[S/C]_{at}^{XPS}$	$[S/C]_{at}^{bulk}$
1	BTX*	-	-	2.0	no meas.	-
2	(BTX)C ₆₀ CS ₂ *	-	-	2.0	>0.005	0.012
3	(BTX)C ₇₀ CS ₂ *	-	-	2.2	>0.005	0.010
4	EDT-TTF	163.8	2.4	2.0	0.726	0.748
5	(EDT-TTF) ₂ C ₆₀ CS ₂	163.9	2.5	2.0	0.102	0.200
6	(EDT-TTF)C ₆₀ C ₆ H ₆	163.9	2.5	2.1	0.030	0.081
7	DB-TTF	164.0	2.4	2.2	0.277	0.286
8	(DB-TTF)C ₆₀ C ₆ H ₆	164.3	2.4	2.0	0.036	0.050
9	EDY-BEDT-DT	163.6	2.4	2.0	0.551	0.670
10	(EDY-BEDT-DT)C ₆₀ C ₆ H ₆	164.0	2.5	2.0	0.075	0.102
11	TMDTDM-TTF	163.7	2.4	2.0	no meas.	0.500
12	(TMDTDM-TTF) ₂ C ₆₀ (CS ₂) ₃ 2	163.8	2.5	1.9	0.094	0.207
13	BEDO-TTF	163.3	2.6	2.6	no meas.	0.333
14	(BEDO-TTF) ₂ C ₆₀	164.0	2.6	2.3	0.079	0.095
15	4MT	163.0	2.7	2.8	0.102	0.125
16	(4MT) ₂ C ₆₀ C ₇ H ₈	163.9	2.7	2.4	0.038	0.040
17	BNDY	164.5	2.9	2.3	0.202	0.182
18	(BNDY)C ₆₀	164.9	2.6	2.0	0.052	0.056

Table 1. Parameters of the XPS spectra of the crystals under study: binding energies S2p; full-widths at half-maximum (Δ) of the main peaks S2p and C1s. The $[S/C]_{at}^{XPS}$ ratios are calculated from the integral intensities of S2p and C1s lines. The $[S/C]_{at}^{bulk}$ ratios determined from the data on the chemical analysis are presented as well. *For the $E_b(\text{Te3d5/2})$ binding energy see the text.

of the $[S/C]$ ratio performed under the assumption that all molecules of the solvent are absent in the zone of analysis, yields the value of 0.150. Therefore, the (TMDTDM-TTF)₂ C₆₀ (CS₂)₃ crystals are characterized not only by the desorption of CS₂ from the subsurface layer, but also by the reduction of the D/F ratio in this layer.

The complexes with such a donor as 4MT may be given as an example where the S/C ratio on the surface practically coincides with that in the bulk (see the Table).

In (BNDY) (C₆₀) crystals the S/C ratio on the surface is also quite close to that in bulk. However, in the S2p spectrum a peak with $E_b(\text{S2p}) = 169.8$ eV (Fig. 2) is observed in addition to the main peak which slightly shifted to higher

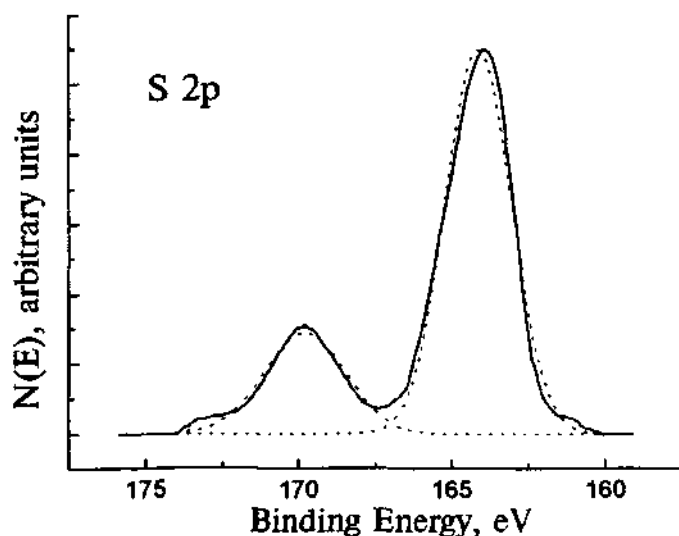


Figure 2. S2p X-ray photoelectron spectrum of (BNDY) (C_{60}). The dotted curves show the best fit by the Gaussians.

binding energies relative to the position of this peak in the pure donor. This peak is absent in the spectra of the pure ligand and the ligand crystallized from the solvent under the conditions similar to those of the growth of (BNDY) (C_{60}) crystals.

For some fullerene compounds with sulphur-containing donors the position of the S2p line on the scale of binding energies practically coincides with that for the initial donor (within the experimental accuracy (± 0.1 eV)). This possibly evidences a weak charge transfer in the course of complex formation. However, for the other complexes (see, for example, $(4TM)_2 C_{60} C_7H_8$) the chemical shift of the S2p line reaches 0.9 eV which is obviously an appreciable effect. We shall notice here that the IR spectra in this and in other cases show the typical structure of the absorption bands corresponding to oscillation modes of solid C_{60} with very insignificant (no more than 1 cm^{-1}) changes of bands positions [5,15,16]. Hence, the measured XPS binding energies can affect not only the charge distribution, but the difference between the surface and the bulk as well. It should be noted that the calibration of the spectra by the Cl1s peak has some essential limitations, especially in the case of carbon containing samples. Thus, for the complexes the Cl1s line intensity is mainly determined by the fullerene molecules, while in the case of spectra of pure donors the main contribution to intensity of this line may be made by carbon atoms with nonzero charge.

The confirmation of this assumption can be seen from the comparison of the parameters ΔS_{2p} which as a rule prove to be lower for the complexes than for appropriate individual donors.

It is found that:

1. The molecules of a solvent (for example, CS_2) incorporated in crystals of the compounds under study are easily desorbed from the subsurface layers of the crystals under the experimental conditions (vacuum, X-ray irradiation);
2. In some cases the donor/fullerene ratio on the surface can essentially differ from that in the bulk according to the data of chemical and/or X-ray structural analyses;
3. Various oxidation states of donor heteroatoms which are not observed in the bulk, may be realized on the crystal surface.

All these points should be considered first of all in the study of the electronic structure of fullerene compounds with organic donors by X-ray photoelectron spectroscopy, electron energy-loss spectroscopy, Auger spectroscopy and other surface methods.

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