

Surface oxidation of donor heteroatoms in crystalline fullerene-donor compounds

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Abstract.

The studies of X-ray photoelectron spectra of a series of crystalline fullerene molecular complexes, $(D)_x(F)(R)_y$, showed that in addition to the main state of a heteroatom of donor, there are heteroatoms in higher oxidation states on a crystal surface. The causes for donor oxidation and the appearance of heteroatoms in higher oxidation states are discussed.

Keywords: Fullerene C_{60} , Charge transfer complexes, Oxidation.

1. Introduction.

Now a great number of fullerene compounds are obtained with a noticeable share of molecular complexes $(D)_x(F)(R)_y$, where F is fullerene C_{60} or C_{70} , D is a donor, and R is a solvent. The donors may be either inorganic (S_8 [1], S_4N_4 [2] or organic (BEDT-TTF [3,4], BEDO-TTF [4,5], BNDY [5], and BTX [6]. These molecular complexes are characterized by weak charge transfer which is reflected in small (within 2 cm^{-1}) shifts of absorption bands in IR spectra attributed to vibrations in fullerene molecule [2,7]. The results of the studies of such compounds by X-ray photoelectron spectroscopy also evidence weak charge transfer at complex formation [8,9]. Crystal structure was solved for some complexes [2,6].

In the present paper we report the results of the study of the surface of $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$, $BNDY \cdot C_{60}$, $(BEDO-TTF)_2 \cdot C_{60}$, $(BEDO-TTF) \cdot C_{60} \cdot C_6H_6$, and $(S_4N_4)_{0.9} \cdot C_{60} \cdot (C_6H_6)_{1.1}$ crystals by X-ray photoelectron spectroscopy.

2. 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(telluraxantenyl) (BTX); bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF), binaphto[1,6-d,e]-1,3-dithiene-2-ylidene (BNDY) and S_4N_4 .

X-ray photoelectron spectra (XPS) were excited by $MgK\alpha$ -radiation ($h\nu = 1253.6\text{ eV}$). The spectra were calibrated as to the peak C1s (285.0 eV). This value corresponds to the position of C1s peak for pure C_{60} and coincides with the data for C_{60} films deposited on different supports [10]. 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.

3. Results and discussion

Figure 1 shows the spectra Te3d for the $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ crystals together with those for an individual donor and the $BTX \cdot C_{60} \cdot CS_2$ crystals. The peak $Te3d_{5/2}$ in the spectrum of

$BTX \cdot C_{60} \cdot CS_2$ is shifted by 0.4 eV with respect to that in pure BTX. The spectra Te3d of all investigated $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ crystals contain the additional peaks, shifted by $\sim 2\text{ eV}$ to higher energies from Te^{2+} peaks. The positions of the additional peaks

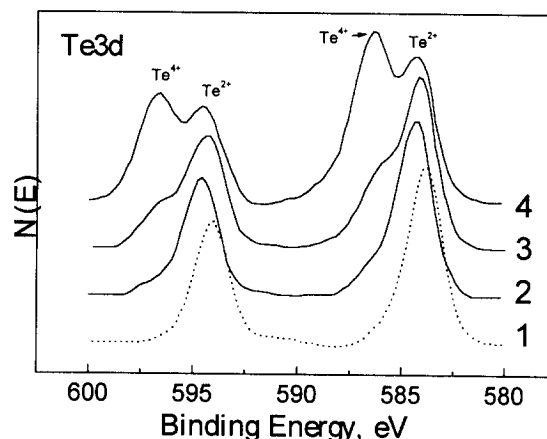


Fig.1. X-ray photoelectron spectra Te3d of BTX (1), $BTX \cdot C_{60} \cdot CS_2$ (2), and $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ (3,4) crystals after the subtraction of a linear background and the normalization to peak intensity.

correspond to Te^{4+} . At the same time the X-ray analysis of the $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ complex shows the conformation of BTX not to differ from that in the $BTX \cdot C_{60} \cdot CS_2$ crystals [6]. The IR spectra of $BTX \cdot C_{60} \cdot CS_2$ and $BTX \cdot C_{70} \cdot (CS_2)_{0.5}$ also did not exhibit an essential difference between the positions of absorption bands attributed to the vibrations of donor atoms [7]. Therefore the Te^{4+} state relates to a thin subsurface layer and its total concentration is small enough to be found in the IR spectra.

Figure 2 demonstrates the XP S2p spectrum of $BNDY \cdot C_{60}$ crystals. The spectrum consists of two peaks, namely, the main peak with the binding energy (E_b) equal to 164.1 eV and the additional one with $E_b = 169.8\text{ eV}$. The position of the additional peak corresponds to the state S^{6+} [9]. It should be noted that the additional peak is absent in the spectrum of the starting BND and in that of BND

Y taken from the checking experiment (crystallization in benzene under the conditions similar to those for BNDY-C₆₀ crystal growth).

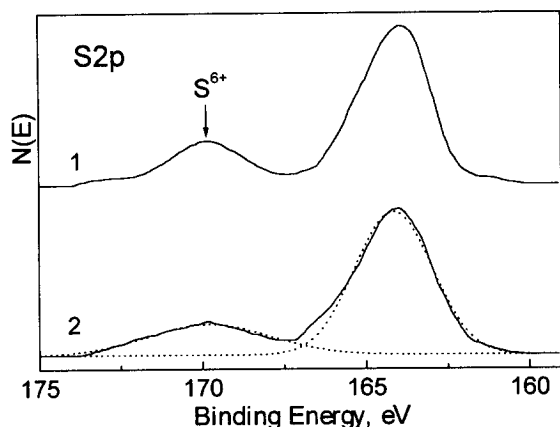


Fig.2. X-ray photoelectron spectra S2p of BNDY-C₆₀(1) and (BEDO-TTF)₂-C₆₀-C₆H₆(2). The dotted curves show the fit by the Gaussians.

The additional peak with $E_b(\text{S}2p)=169.8$ eV was also found in the XP spectrum of the (BEDO-TTF)₂-C₆₀-C₆H₆ crystals. In this case the main peak was observed at $E_b=164.2$ eV. At the same time the spectra of the individual donor and the (BEDO-TTF)₂-C₆₀ complex synthesized in CS₂ demonstrated no peaks which can be attributed to S⁶⁺.

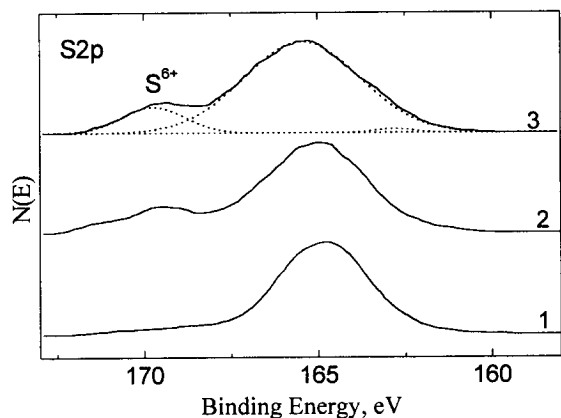


Fig.3. X-ray photoelectron spectra S2p of S₄N₄ (1), (S₄N₄)_{0.9}-C₆₀-(C₆H₆)_{1.1} (2) and the product of S₄N₄ interaction with C₆₀ which was isolated by evaporation of the solvent in inert atmosphere (3).

Tetrasulfur tetranitride is known to decompose slowly in storage. Therefore tetrasulfur tetranitride was recrystallized from 1,2-dichloroethane immediately before the preparation of the S₄N₄ complex with C₆₀. The spectrum S2p of the (S₄N₄)_{0.9}-C₆₀-(C₆H₆)_{1.1} crystal (Fig.3) shows a quite intensive peak S2p with $E_b \approx 169.5$ eV which corresponds to S⁶⁺. For the product of S₄N₄ interaction with C₆₀ isolated by the evaporation of the solvent (benzene) in inert atmosphere a relative intensity of the peak S⁶⁺ only somewhat decreases.

It should be noted that the effect of oxidation is observed only for a small number of donors. For example, no sulfur in high oxidation states was found on the surface of the DBTTF-C₆₀-C₆H₆, DBTTF-C₇₀-C₆H₆, EDY-BEDT-DT-C₆₀-C₆H₆, (TMDTDM-TTF)₂-C₆₀(CS₂)₃ and other crystals[9], where DBTTF is dibenzotetrathiafulvalene, EDY-BEDT-DT is 2,2'-ethanedithyldiene-bis(4,5-ethylenedithio-1,3-dithiol), and TMDTDM-TTF is tetramethylenedithiodimethyltetrathiafulvalene.

Thus, all fullerene compounds with the above donors demonstrate the similar effect which consists in that a part of heteroatoms is in high oxidation state on the surface of the crystals. The individual donors (BTX, BNDY, and BEDO-TTF) are usually quite resistant to oxygen at long-duration storage in air under normal conditions or in slow crystallisation under conditions of the complex preparation.

For some donors reported in the present paper there are the reactions with the formation of heteroatoms in high-oxidation states. Such a reaction is characteristic of Te organic compounds. For example, BTX in benzene solution may attach iodine with the formation of (BTX)I₄ in which iodine is bound to Te atom (Te⁴⁺ state) [11]. S₄N₄ may be oxidized by an aqueous solution of chloramine-T to ammonia and sulfuric acid [12]. Individual solid fullerene is known to adsorb oxygen (up to 5 O₂ molecules per one fullerene molecule [13]). It is obvious that the appearance of high-oxidation states of donors on the surface of the complex crystals is associated with the presence of fullerene which performs as a catalyst and/or a carrier of active oxygen. Donor coordination with fullerene molecule containing adsorbed oxygen may provide donor oxidation even at room temperature. The other cause of donor oxidation may be its activation due to donor-C₆₀ interaction in the complex.

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