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SYNTHESIS AND SOME PROPERTIES OF CHARGE TRANSFER COMPLEXES OF C_{60} WITH ASYMMETRIC DONORS OF TETRATHIAFULVALENE FAMILY

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Abstract—New charge transfer complexes: (TMDTDM-TTF)$_2$C$_{60}$(CS$_2$)$_3$, TMDTDM-TTF•C$_{60}$•C$_6$H$_6$, (EDT-TTF)$_2$C$_{60}$CS$_2$ were synthesized by the reaction of C$_{60}$ with asymmetric donors in CS$_2$ and benzene. XPS- and IR-spectroscopy show a weak charge transfer in these compounds. The influence of the solvents during the formation of the complexes was disscussed. The (TMDTDM-TTF)$_2$C$_{60}$(CS$_2$)$_3$ crystal structure reveals that it has a layered structure with alternating sheets of C$_{60}$ and donor dimers. © 1997 Elsevier Science Ltd.

Keywords: fullerene C$_{60}$, asymmetric tetrathiafulvalenes, TG-analysis, IR-, X-ray photoelectron spectroscopy, charge transfer complexes

1. INTRODUCTION

The discovery of optical, superconducting and magnetic properties in fullerene compounds [1–3] evoked a great interest to the synthesis of ion-radical salts and charge transfer complexes of fulleren. As a result, a series of fullerene compounds with organic donors of different classes were obtained [4, 5]. These compounds are most symmetrical donors of the TTF-family: bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF)$_2$C$_{60}$ [6], octamethylenetetrathiafulvalene (OMTTF)(C$_{60}$)C$_6$H$_6$ [7] and others [8, 9]. Only one of the fullerene complex with asymmetric donor: EDT-TTF ~C$_{60}$ was isolated from benzene [7]. The utilization of different types of donors allowed the synthesis of the compounds with various C$_{60}$ packing in a crystal and the consequently different properties of the compounds obtained.

Here we report on the synthesis and some of the characteristics of charge transfer complexes of C$_{60}$ with the asymmetric organic donors (Fig. 1) tetramethylenedithiodimethyltetrathiafulvalene: (TMDTDM-TTF)$_2$ C$_{60}$(CS$_2$)$_3$ (I), TMDTDM-TTF•C$_{60}$•C$_6$H$_6$ (II), ethylenedithiotetrathiafulvalene (EDT-TTF)$_2$C$_{60}$CS$_2$ (III), EDT-TTF·C$_{60}$•C$_6$H$_6$ (IV) and the crystal structure of (TMDTDM-TTF)$_2$C$_{60}$(CS$_2$)$_3$.

2. EXPERIMENTAL

The compounds I and III were obtained by the evaporation of C$_{60}$ and donor solution in carbon disulfide at 1:2 molar ratio for 5 days at room temperature. The crystals of I were formed with 30% yield as black parallelipipeds up to 2 mm in size together with the adduct C$_{60}$(CS$_2$)$_x$, which was formed as elongated plates. The crystals of I were separated manually from the adduct ones by using a microscope. The crystals of III were obtained with 80% yield as black plates of 1 mm size. Then I and III were separated from the donor by washing with tetrahydrofuran and subsequently they were washed with ether. The composition of the complex I: (TMDTDM-TTF)$_2$ C$_{60}$(CS$_2$)$_3$ was defined by single crystal X-ray study [8]. The thermogravimetry revealed that the solvent is released from the crystals at temperatures ranging from 355 K up to 475 K which is above the boiling point of CS$_2$. A partial decomposition of the donor TMDTDM-TTF begins from 540 K and is consistent with the decomposition temperature of the individual donor. The loss of a mass after 1075 K is due to the C$_{60}$ sublimation.

Elemental analysis showed that the compound III was a 1:2 complex of C$_{60}$ with EDT-TTF: C$_{77}$H$_{12}$S$_{13}$. Calculated: C 66.87, H 0.86, S 32.27. Found C 67.03, H 1.35, S 31.23. The thermogravimetry showed, that the solvent CS$_2$ is released from the crystals at temperatures ranging from 380 K to 440 K (6% of total mass). A partial decomposition of the donor EDT-TTF begins from 565 K and is consistent with the decomposition temperature of the individual donor. The loss of a mass after 975 K is due to the C$_{60}$ sublimation. Thus the composition of the complex is (EDT-TTF)$_2$C$_{60}$•CS$_2$.

The compounds II and IV were obtained by the evaporation of C$_{60}$ and corresponding donor solutions in benzene at 1:1 molar ratio for 7 days at room temperature. The crystals of II were formed with 70% yield as black prisms. The crystals of IV were obtained with 70% yield as needles. Elemental analysis showed that the compounds II and IV were a 1:1:1 complex of C$_{60}$, donor and benzene. For II, C$_{73}$H$_{20}$S$_6$: Calculated C 81.57, H 1.73, S 16.70. Found C 80.94, H 1.55, S.17.82. For IV, C$_{69}$H$_{12}$S$_6$: Calculated, C 80.88, H 1.30, S 17.82. Found, 80.03, H 1.51, S 17.83.

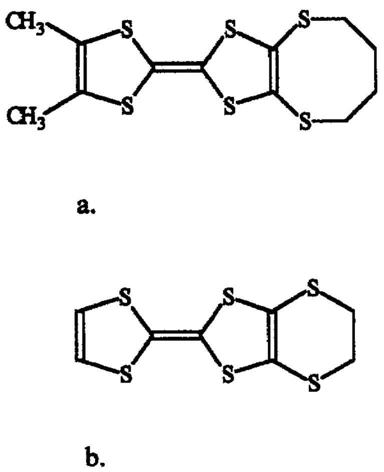

Fig. 1. Molecular structures of the donor TMDTDM-TTF (a) and EDT-TTF (b) molecules.

The IR-spectroscopy (tablets in KBr) showed that there are absorption bands of C_{60} and donors in the IR spectra of I–IV. The positions of the absorption band attributed to C_{60} are 1428, 1182, 577, 527 cm^{-1}. The absorption bands at 2919, 2850, 1460, 1429, 1182, 776, 749, 722, 623, 454 cm^{-1} in I and 2919, 1460, 1429, 1182, 779, 745, 623 in II belong to the oscillation modes of TMDTDM-TTF. The absorption bands at 2950, 1405, 1285, 1255, 1086, 792, 775, 650 cm^{-1} in III and 1405, 1255, 795, 780, 644 cm^{-1} in IV belong to the oscillation modes of EDT-TTF. The absorption band at 1508 cm^{-1} in I and III corresponds to the oscillation mode of CS_2 and that at 676 cm^{-1} in II and IV corresponds to the oscillation mode of C_6H_6 molecules.

3. RESULTS AND DISCUSSION

For the $(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ the crystal data are: $C_{87}H_{28}S_{18}$, $M = 1650.17$, monoclinic, space group $C2$, $a = 15.174(3)$, $b = 13.313(3)$, $c = 16.762(3)$ Å, $\beta = 103.17(3)°$, $V = 3297.1(11)$ Å^3, $Z = 2$, $D_c = 1.662$, T = 153(2) K, R = 5.97% [8].

The projection of the crystal structure along the *b* axis is shown in Fig. 2. C_{60} molecules are arranged in distorted hexagonal layers in the *a*0*b* plane with the distances between the centres of the fullerene spheres along the *b* axis and along the *ab* diagonal equal to 13.31 and 10.09 Å, respectively. Each C_{60} sphere is sandwiched between two donor molecules. The efficient packing is provided by a 'concave' conformation of the TMDTDM-TTF molecule. The dihedral angles between the central tetrathiafulvalene core and the outer tetramethylene-dithio- and dimethyl-planes of the donor are 27.7° and

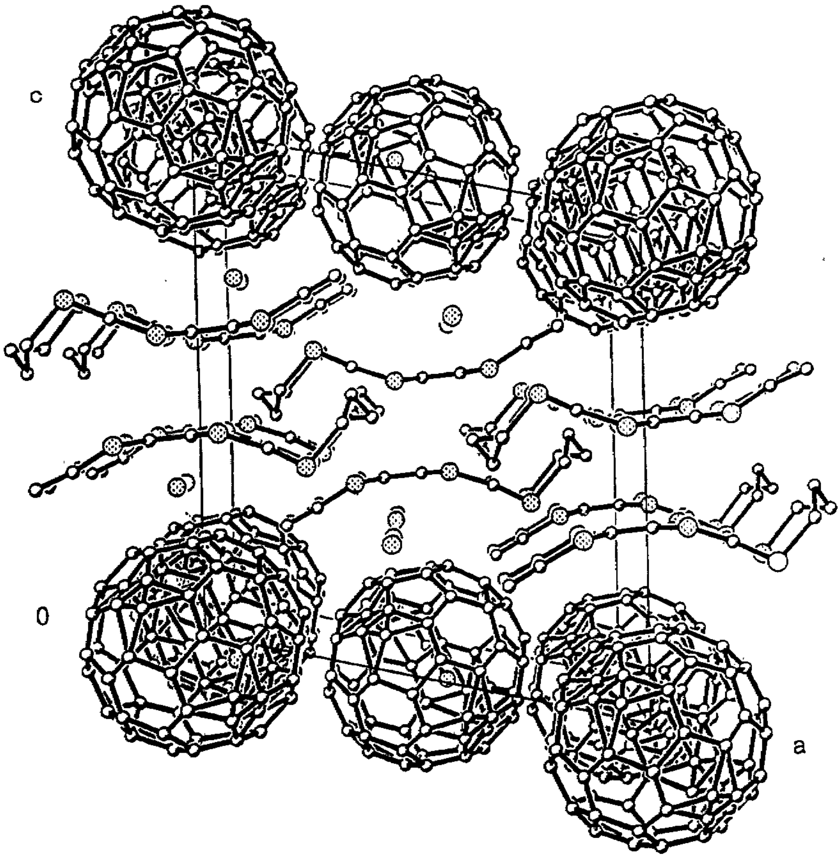

Fig. 2. Projection of the crystal structure of $(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ along the *b* axis.

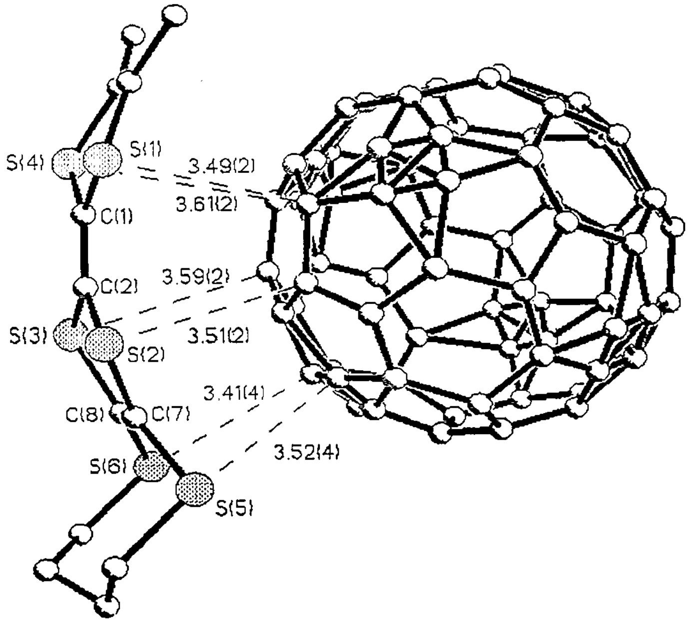

Fig. 3. Disordered C_{60} and one of two closest TMDTDM-TTF molecules with the shortest S(donor)... C(C_{60}) contacts.

23.6° respectivly. The donor molecules packed head-to-tail form the dimers with the intermolecular contacts S...S equal to 3.7–3.8 Å (sum of van der Waals radii of two sulfur atoms 3.70 Å). These dimers form two-dimensional layers with S...S contacts between them are equal to 3.840 Å, so that the whole packing pattern may be described as the alternating layers of C_{60} and the dimers of TMDTDM-TTF. The shortest intermolecular contacts C(C_{60})-S(donor) (3.412–3.793 Å) shown in Fig. 3 are close to the sum of van der Waals radii of sulfur and carbon atoms 3.57 Å [10]. The comparison of the central C–C bond length in the donor (1.334 Å in this work) with that in the related (BEDT-TTF)$_2C_{60}$ compound [6] (1.327 Å) indicates a relatively weak charge transfer which does not affect the normal atomic radii in the complex.

The molecules of CS_2 on twofold axes are located between C_{60} molecules in the fullerene layers forming short S···C(C_{60}) contacts of 3.42 Å. The other independent CS_2 molecules (in general positions) incorporated in donor layers have no short contacts in their environment.

The complexes I–IV have two different donor:C_{60} ratios. The complexes of 2:1 ratio (I and III) and the 1:1 ratio (II and IV) prepared from carbon disulfide and benzene, respectively. The complexes with the 2:1 ratio possess a sandwich structure like the stuctures of (TMDTDM-TTF)$_2C_{60}(CS_2)_3$ and (BEDT-TTF)$_2C_{60}$ [6] where two flexibile donor molecules are coordinated with one C_{60} molecule. Such complexes were mainly obtained from CS_2 which obviously promotes the formation of such structures.

If the donor molecule is not flexible as bis(ethylenethio)tetrathiafulvalene BET-TTF [11] and OMTTF [7], the coordination with the fullerene molecule is not realized through a sandwich type. One occured with the preservation of the planarity of the donor molecule with 1:1 composition probably possessing OMTTF·C_{60}·C_6H_6 [7] type structure. The formation of these complexes is promoted by benzene which has a flat structure.

X-ray photoelectron spectroscopy data for (TMDTDM-TTF)$_2C_{60}(CS_2)_3$ (I), (EDT-TTF)$_2C_{60}CS_2$ (III) and EDT-TTF•C_{60}•C_6H_6 (IV) and corresponding donors TMDTDM-TTF and EDT-TTF are presented in Table 1. The energies of S2p band for the complexes are close to those of the individual donors, which indicates a small charge transfer in these complexes. The halfwidths

Table 1. X-ray photoelectron spectroscopy data for (TMDTDM-TTF)$_2C_{60}(CS_2)_3$ (I), (EDT-TTF)$_2C_{60}CS_2$ (III), EDT-TTF•C_{60}•C_6H_6 (IV) and corresponding donors TMDTDM-TTF and EDT-TTF

The sample	The halfwidth of the peak C1s (eV)	The halfwidth of the peak S2p (eV)	The energy of S2p band (±0.1 eV)	[S/C] ^{XP}, at.
TMDTDM-TTF	2.0	2.4	163.7	—
I	1.9	2.5	163.8	0.09
EDT-TTF	2.0	2.4	163.8	—
III	2.2	2.5	163.9	0.11
IV	2.1	2.5	163.9	0.04

of the peak S2p (2.5 eV) for I and III and the $[S/C]^{XP}$ at. ratios are equal to 0.09 and 0.11 for I and III, respectively, calculated from the ratio of the integral intensities of the peak S2p and C1s in XP-spectra of the complexes in terms of Scofield's data [11]. It is obvious that CS_2 is removed from the zone of the analysis in the registration conditions (high vacuum and X-ray radiation). A related effect (the elimination of CS_2 molecules under vaccum) was previously observed for the complex $TPDP(C60)_2(CS_2)_4$, where TPDP is tetraphenyldipyranylidene [12].

According to IR-spectroscopy data for $(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ (tablets in KBr), the positions and the ratio of the intensities of the absorption bands attributed to C_{60}: 1428, 1182, 577, 527 cm^{-1} remained unchanged with respect to the individual C_{60} and indicated a small charge transfer for this compound. The comparison of the absorption bands of TMDTDM-TTF at 2919, 2850, 1460, 1429, 1182, 776, 749, 722, 623, 454 cm^{-1} in I with the absorption band for the individual donor 2908, 2845, 1486, 1436, 1299, 1283, 1181, 1086, 890, 865, 775 cm^{-1} showed the disappearance of some absorption bands and the shifts of other bands. These changes have probably resulted from the breakdown of the planarity of the donor molecule by its coordination with C_{60}.

The UV-VIS-NIR optical absorption spectrum of $(TMDTDM\text{-}TTF)_2C_{60}(CS_2)_3$ [13] shows a wide band at 900 nm associated with charge transfer from TMDTDM-TTF to fullerene.

The conductivity of I measured by a standard two-probe method yielded the value 10^{-6} $(\Omega{\cdot}cm)^{-1}$.

4. CONCLUSION

New charge transfer complexes of C_{60} with asymmetric donors of the tetratiafulvalene family were obtained. Depending on the carrying out of the reaction these were charge transfer complexes of fullerene. In carbon disulfide or benzene solutions the compounds with the (donor: C_{60}) 2:1 and 1:1 ratio, respectively, were formed The application of flexible asymmetric donor molecules capable of the head-to-tail packing allowed one to obtain the complex with two-dimensional closely packed layers of fullerenes and donor molecules. The presence of solvent molecules which can easily be removed from the complexes allows one to dope it with different dopants [14] in order to increase the charge transfer degree.

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