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Synthesis, crystal structure and some properties of charge transfer complex of C_{60} with asymmetric donor TMDTDM–TTF

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Abstract

The reaction of C_{60} with asymmetric donor tetramethylenedithiodimethyl–tetrathiafulvalene (TMDTDM–TTF) in CS_2 yields the $(TMDTDM–TTF)_2C_{60}(CS_2)_3$ (**I**) molecular complex. The study of the crystal structure of **I** reveals that it has a layered structure with alternating sheets of C_{60} and donor dimers. X-ray photoelectron spectroscopy (XPS) and IR spectroscopy show a weak charge transfer in this compound.

Keywords: Single-crystal growth; Infrared and Raman spectroscopy; Photoelectron spectroscopy; X-ray diffraction; Fullerenes and derivatives

1. Introduction

The discovery of superconductivity in fullerene compounds with alkali metals [1,2] and ferromagnetism in C_{60} salts with strong donor TDAE [3] evoked a great interest in the synthesis of ion-radical salts and charge transfer complexes of fullerene. As a result, a series of fullerene compounds with organic donors of different classes was obtained [4,5]. These compounds are mostly symmetrical donors of the TTF class; bis(ethylenedithio)tetrathiafulvalene $(BEDT–TTF)_2C_{60}$ [6], octamethylenetetrathiafulvalene $(OMTTF)(C_{60})C_6H_6$ [7] and others [8]. The utilization of different types of donors allowed the synthesis of compounds with various C_{60} packing in a crystal and, consequently, different properties of the compounds obtained.

Here we report the synthesis, crystal structure and some characteristics of the first charge transfer complex of C_{60} with the asymmetric organic donor tetramethylenedithiodimethyl–tetrathiafulvalene (TMDTDM–TTF, Fig. 1). The single-crystal X-ray study shows the composition of the complex to be $(TMDTDM–TTF)_2C_{60}(CS_2)_3$ (**I**).

2. Results and discussion

Compound **I** was obtained by the evaporation of C_{60} and TMDTDM–TTF solution in carbon disulfide at a 1:2 molar ratio for 5 days at room temperature. Single crystals of **I** were formed with 30% yield as black parallelepipeds of sizes up to 2 mm, together with the adduct $C_{60}(CS_2)_x$ which was formed as elongated plates. Crystals of **I** were separated manually from those of the adduct by using a microscope. Compound **I** was separated from the donor by washing with tetrahydrofuran and then with ether.

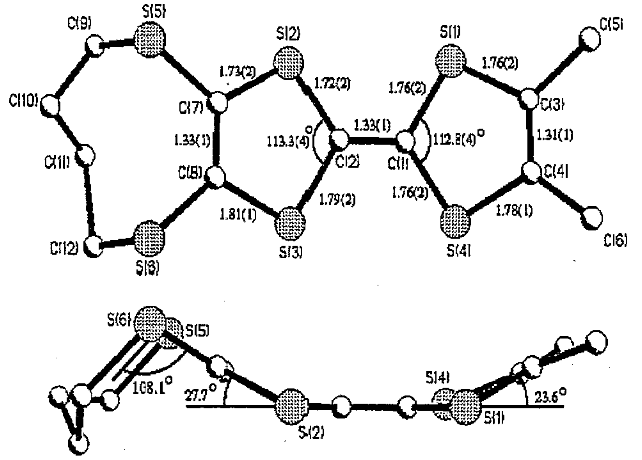

Fig. 1. Molecular structure of the donor TMDTDM–TTF with the main geometric parameters.

IR spectroscopy (tablets in KBr) of **I** shows that the frequencies and the ratio of the intensities of the absorption bands, attributed to C_{60} (1428, 1182, 577, 527 cm^{-1}), remain

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unchanged with respect to the individual C_{60}. The absorption bands at 1460, 1429, 1182, 776, 749, 722, 623, 454 cm^{-1} belong to the oscillation modes of TMDTDM–TTF (the individual donor has the following absorption bands: 1486, 1436, 1299, 1283, 1181, 1086, 890, 865, 775 cm^{-1}). The disappearance of some absorption bands and the shifts of other bands are probably associated with a breakdown of the planarity of the donor molecule by its coordination with C_{60}. The absorption band at 1508 cm^{-1} corresponds to the oscillation mode of CS_2.

According to X-ray photoelectron spectroscopy (XPS) data the energy of the S(2p) band (163.8 ± 0.1 eV) for the complex does not differ from that of the individual TMDTMD–TTF (163.7 ± 0.1 eV) which indicates no charge transfer from the donor. Nevertheless, the UV–Vis–NIR optical absorption spectrum of $(TMDTDM\text{–}TTF)_2C_{60}(CS_2)_3$ shows a wide band at 900 nm associated with charge transfer from TMDTDM–TTF to fullerene.

Thermogravimetry revealed that the solvent is released from the crystals at temperatures from 355 up to 475 K which are above the boiling point of CS_2. According to X-ray data a wide temperature range for CS_2 elimination is conditioned by two positions of CS_2 molecules with different degrees of coordination. 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 mass after 1075 K is due to the C_{60} sublimation.

The crystal structure [1] of **I** reveals that one C_{60} and one carbon disulfide molecule are placed in special positions on the twofold axis, while the donor TMDTDM–TTF and two other CS_2 molecules occupy general positions.

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 *a0b* plane with the distances between the centres of 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 (Fig. 1). The dihedral angles between the central TTF core and the outer tetramethylenedithio and dimethyl planes of the donor are 27.7 and 23.6°, respectively, which is similar to donor molecule conformation in $(BEDT\text{–}TTF)_2C_{60}$ [6] and $(BDMT\text{–}TTeF)\text{-}(C_{60})CS_2$ [8] complexes. The donor molecules packed head-to-tail form the dimers with the intermolecular S···S contacts equal to 3.7–3.8 Å (the 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 equal to 3.840 Å, so that the whole packing pattern may be described as 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 [9]. The comparison of the central C–C bond length in the donor (1.334 Å in this work) with that in the related $(BEDT\text{–}TTF)_2C_{60}$ compound [6] (1.327 Å) indicates a relatively weak charge transfer which does not affect the normal atomic radii in the complex.

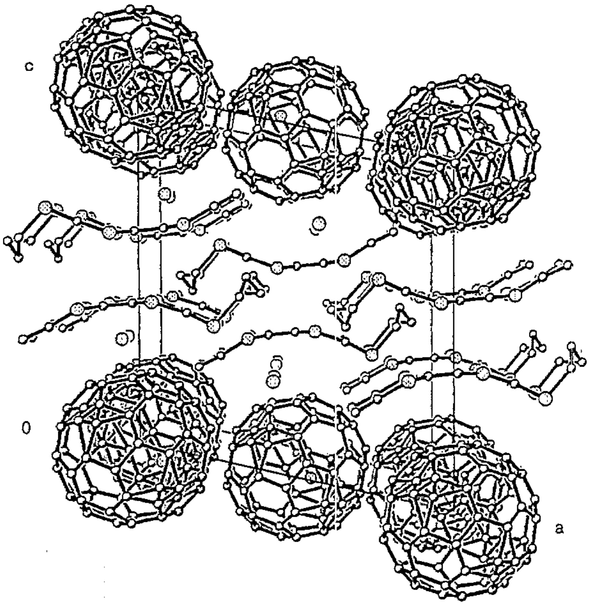

Fig. 2. Projection of the crystal structure of $(TMDTDM\text{–}TTF)_2C_{60}(CS_2)_3$ along the *b* axis.

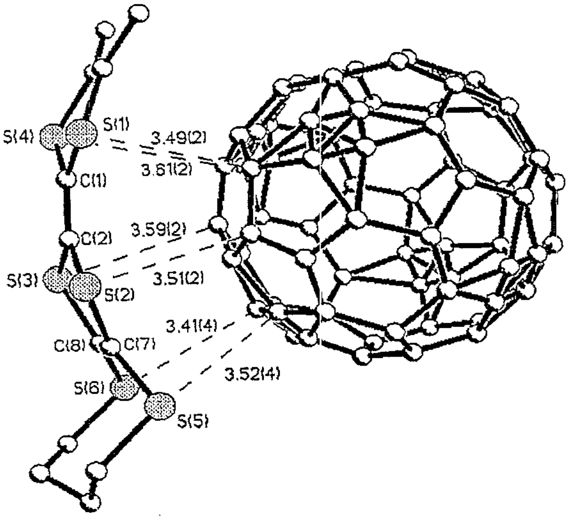

Fig. 3. Disordered C_{60} and one of two closest TMDTDM–TTF molecules with the shortest S(donor)···$C(C_{60})$ contacts. The second TMDTDM–TTF molecule, revealed by the twofold symmetry axes passing through C_{60} moiety, is not shown.

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[1] Crystal data: $C_{87}H_{28}S_{18}$, $M = 1650.17$, 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, $Z = 2$, $D_c = 1.662$, $F(000) = 1676.0$. Mo Kα radiation (graphite monochromator, $\lambda = 0.710\,73$ Å, $\mu = 0.64$ mm^{-1}), $T = 153(2)$ K. Single-crystal X-ray diffraction (XRD) data were collected at 152 K on a Siemens P3/PN diffractometer at the Centre for X-ray Structural Studies, Institute of Organoelement Compounds. 4252 reflections with $2 < \theta < 44°$ were collected. The structure was solved by direct methods by using SHELXS-86 and refined by using SHELXL-93 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and refined isotropically. Finally, $R = 5.97\%$, $R_w = 11.67\%$ for 2103 reflections ($F_o > 2\sigma(F)$).

Atomic coordinates, bond lengths, bond angles and thermal parameters are deposited at the Cambridge Crystallographic Data Centre.

The molecules of CS_2 on twofold axes are located between C_{60} molecules in the fullerene layers forming short $S\cdots C(C_{60})$ 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 fullerene molecules are statistically disordered in the same manner as it was found in the XRD study of the $Ph_4PC_{60}\cdot Ph_4PCl$ [10] complex fulleride. There are two half-occupied orientations, which transform to one another by a molecular rotation about the twofold crystallographic axis which crosses two opposite 6–5 bonds in the C_{60} moiety. The refinement of the positions of fullerene carbon atoms with the anisotropic temperature factors resulted in the coalescense of their close positions in two disordered orientations (except the characteristic 'crosses' placed in octahedrally arranged sites), yielding the averaged values for C–C bond lengths in fullerene. However, this refinement significantly improved the accuracy of the geometrical parameters in the TMDTMD–TTF donor molecule.

Conductivity measured by a standard two-probe method yielded the value 10^{-6} S cm^{-1}; thus **I** is an insulator.

The complex **I** is therefore to be considered as a van der Waals compound with a weak charge transfer. This may be explained by a relatively small electron donor ability of TMDTDM–TTF. Obviously, the application of asymmetric donor molecules capable of bending and arranging in a head-to-tail configuration allows one to obtain the complex with two-dimensional layers of fullerenes and donor molecules. As a result, a densely packed complex with close contacts (less than or equal to the sum of the van der Waals radii between the components) was obtained. The presence of solvent molecules, easily removed from the complex, allows it to be doped with different dopants [11] in order to increase the charge transfer degree. The study of the doping of this compound is in progress.

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