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Synthesis and crystal structure of a C_{60} complex with a bis(ethylenedithio)tetrathiafulvalene radical cation salt: $(\text{BEDT-TTF}\cdot I_3)C_{60}$

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This communication describes a novel solid, crystals of which are grown by a diffusion technique, consisting of alternating fullerene and radical cation salt layers.

Fullerenes are known to form only neutral molecular complexes with the tetrathiafulvalene derivatives (TTFs†): $(\text{BEDT-TTF})_2C_{60}$;[1] $\text{OMTTF}\bullet C_{60}\cdot C_6H_6$;[2] $\text{DBTTF}\cdot C_{60}\cdot C_6H_6$[3] and some others.[2,3] The lack of charge transfer defines the dielectric properties of these complexes.[2,3] On the other hand, TTF radical cation salts with different inorganic and organic anions demonstrate metallic and superconducting properties.[4] An example is a series of the BEDT-TTF salts with linear and polymeric anions which possess superconducting properties: $(\text{BEDT-TTF})_2X$, $X = I_3^-$, IBr_2^-, AuI_2^-, ReO_4^-, $Cu(NCS)_2^-$ and $(\text{BEDT-TTF})_4Hg_{2.89}Hal_8$, Hal = Cl, Br.[4] Since the properties of radical cation salts are affected by the polarizability of the molecules, we prepared compounds in which the TTF radical cation salts are surrounded by highly polarizable fullerene molecules (α_M = 85 Å^3 for C_{60}).[5]

In previous work we prepared a number of C_{60} neutral complexes and intercalated them by exposure to iodine vapor. The iodine replaces a solvent molecule and oxidizes a donor to a radical cation to form $(D^{\cdot+}I_n^-)C_{60}$, where $n \leqslant 5$ and D = DBTTF, TPDP or TMDTDM-TTF.[6] The intercalation process results in an increase of the conductivity of the complexes by 1–3 orders of magnitude. However, the diffusion process of intercalation does not allow synthesis of crystals with homogeneously distributed iodine. Therefore, we tried to synthesize such three-component compounds in solution. We reported earlier that cocrystallization of $\text{BEDT-TTF}\cdot I_{3.5}$ in a saturated fullerene solution in a chlorobenzene–benzonitrile (1:5) mixture yielded (small) single crystals of $(\text{BEDT-TTF}\cdot I_3)C_{60}$.[7] However, the crystals were not of adequate size to allow crystal structure determination.

Here we report the first crystal structure of $(\text{BEDT-TTF}\cdot I_3)C_{60}$ and a new general synthetic procedure for C_{60} complexes comprising radical cation salts of donors. The procedure allows the complexes to be prepared as single crystals suitable for diffraction studies.

$(\text{BEDT-TTF}\cdot I_3)C_{60}$ **1** was prepared by slow diffusion of iodine dissolved in acetonitrile which was layered on a solution of C_{60} and BEDT-TTF (1:1) in a 9:1 toluene–1,2-dichlorobenzene mixture. Crystals of **1** were formed as black hexahedrons on the walls of a flask. Simultaneously, planar rhomb-shaped crystals of β-$(\text{BEDT-TTF})_2I_3$ free of C_{60} crystallize as an admixture.

The technique is based on the insolubility of both the fullerene and the donor radical cation salt $D^{\cdot+}I_n^-$ in acetonitrile. In this case the diffusion of the acetonitrile solution of iodine into the toluene–1,2-dichlorobenzene layer results in the formation of the $(D^{\cdot+}I_n^-)C_{60}$ compound.

Single crystal X-ray diffraction data of **1**‡ shows that C_{60}, $(\text{BEDT-TTF})^{\cdot+}$, and I_3^- are fully ordered, with the fullerene, $(\text{BEDT-TTF})^{\cdot+}$ and I_3^- moieties residing in special positions on two-fold axes. The densely packed C_{60} layers parallel to the *bc* plane alternate with $(\text{BEDT-TTF})^{\cdot+}$, and I_3^- layers. Fig. 1 shows the view of the crystal structure of **1** along the *b* axis.

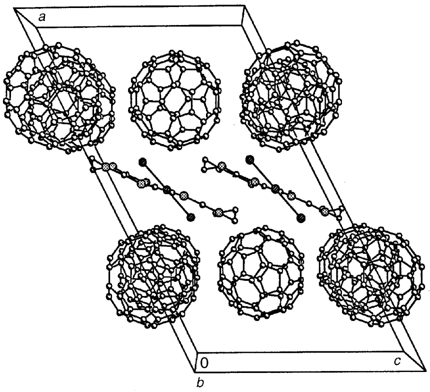

Fig. 1 The projection of the crystal structure of **1** along the *b* axis.

The shortest distance between the centers of the C_{60} molecules in parallel layers is 15.61 Å. Within the layers each C_{60} molecule is surrounded by six adjacent C_{60} molecules with center-to-center distances equal to 9.93–9.97 Å, close to similar distances in neat C_{60} crystals (9.94 Å at 153 K).[8] Adjacent C_{60} molecules within the layers are oriented with the five-membered rings facing each other or with the 6–5 bond of one molecule facing the center of the pentagonal ring of the adjacent molecule, with C···C distances in the range 3.22–3.37 Å.

The ion radical layer (Fig. 2) consists of chains in which the $(\text{BEDT-TTF})^{\cdot+}$ ion alternates with I_3^-. One of the ethylene hydrogen atoms forms short contacts of 3.10(1) and 3.20(1) Å with two iodine atoms (Fig. 2). Adjacent chains are shifted with respect to each other to form a chequer-like arrangement of $(\text{BEDT-TTF})^{\cdot+}$ and I_3^- within the layer. Short van der Waals S···I contacts (3.80–3.96 Å) link two $(\text{BEDT-TTF})^{\cdot+}$ molecules in adjacent chains. The shortest S···S distance between $(\text{BEDT-TTF})^{\cdot+}$ molecules in neighboring chains is 3.75–3.85 Å, which is larger than the sum of the van der Waals radii of two sulfur atoms (3.6 Å).

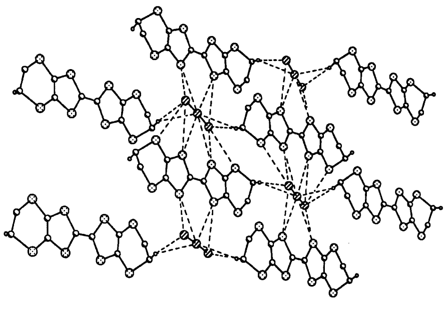

Fig. 2 The projection of the layer comprising $(\text{BEDT-TTF})^{\cdot+}$ and I_3^- on the *bc* plane. Only H-atoms involved into short van der Waals contacts with I_3^- are shown.

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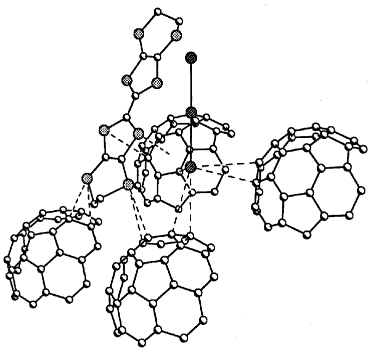

Fig. 3 Short van der Waals contacts between (BEDT-TTF)$^{\cdot+}$, I_3^- and C_{60}. Only the van der Waals contacts with one layer of C_{60} molecules are shown. Similar contacts are formed in the second adjacent layer.

Short van der Waals contacts exist between the C_{60} and the (BEDT-TTF)$^{\cdot+}$/I_3^- layers (Fig. 3). Each (BEDT-TTF)$^{\cdot+}$ and I_3^- form short contacts with three C_{60} molecules in each of the adjacent layers. The S(BEDT-TTF)$\cdots$C(C_{60}) distances (3.25–3.40 Å) in **1** are significantly shorter than those in the C_{60} complexes with neutral tetrathiafulvalenes: 3.446–3.556 Å in (BEDT-TTF)$_2$$C_{60}$;[1] 3.47–3.72 Å in DBTTF•C_{60}•C_6H_6;[3] 3.412–3.793 Å in (TMDTDM-TTF)$_2$$C_{60}$($CS_2$)$_3$.[3] Such shortened contacts of (BEDT-TTF)$^{\cdot+}$ and C_{60} in **1** are a result of the penetration of the (BEDT-TTF)$^{\cdot+}$ molecules into the cavities in the fullerene layers (Fig. 3), while in the C_{60} complexes with neutral TTFs, the TTF molecules envelope the spherical surface of C_{60}. The linear I_3^- anions also extend into the cavities in the C_{60} layers to form five shortened van der Waals I$\cdots$C(C_{60}) contacts [3.77–3.83(3) Å] (Fig. 3).

In contrast to (BEDT-TTF)$_2$$C_{60}$, in which the neutral BEDT-TTF molecule has a 'boat' conformation, (BEDT-TTF)$^{\cdot+}$ has an almost planar shape in **1** (Fig. 4). However, the short contacts with the C_{60} molecules affect the geometry of (BEDT-TTF)$^{\cdot+}$. In contrast to the η-BEDT-TTF·I_3 salt,[9] (BEDT-TTF)$^{\cdot+}$ in **1** has a 'chair' conformation with the fold along the S1–S2 and S1a–S2a vectors, and dihedral angles between the planes $\approx$ 7.4°. The central S_4C_2 fragment of the molecule is not fully planar, but twisted around the double bond. The torsion angle between the plane formed by C1, S1, S2, and C1a, S1a, S2a is 174.1°. The six-membered ring has a sofa conformation, the deviation of the C4 atom from the plane of the other ring atoms being 0.806(4) Å. The central C=C bond length in (BEDT-TTF)$^{\cdot+}$ is 1.402(8) Å, close to that in η-BEDT-TTF·I_3 [1.40(1) Å][9] and corresponding to a +1 charge on (BEDT-TTF)$^{\cdot+}$.

The ordering of the C_{60} molecules in **1** allows their bond lengths to be analyzed. The averaged lengths of the 6–6 and 6–5 bonds of C_{60} are 1.395(5) and 1.449(5) Å, respectively, the values being close to those of the 6–6 and 6–5 bonds in neutral (BEDT-TTF)$_2$$C_{60}$ [1.389(7) and 1.452(1) Å, respectively].[1] The diameters of the C_{60} molecule in three orthogonal directions running through the centers of the oppositely located 6–6 bonds are equal to 6.941, 6.943 and 6.974 Å, thus the deviation from sphericity is only *ca.* 0.03 Å.

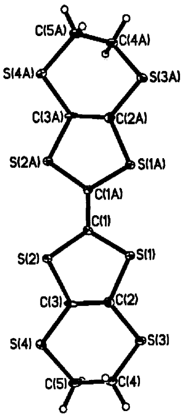

Fig. 4 Geometry of the (BEDT-TTF)$^{\cdot+}$ radical cation in **1**.

Thus, the structure of **1** retains to a great extent the features of the C_{60} structure, with radical cation layers separating the C_{60} layers. The (BEDT-TTF)$^{\cdot+}$ and I_3^- ions interact mostly electrostatically within the layer, while they form van der Waals contacts with fullerene layers.

1 is a semiconductor with σ = 10^{-4} S cm^{-1}. Such behavior is characteristic of simple BEDT-TTF·I_3 salts[9] with an integer charge (+1) on the BEDT-TTF molecule. In the current structure it can be associated also with the nature of the radical cation layer, in which there is no overlap of the π-orbitals of the (BEDT-TTF)$^{\cdot+}$ radical cations. It is known that BEDT-TTF salts with a formal charge of +0.5 show higher conductivity. However, the compound of composition ((BEDT-TTF)$_2$$I_3$)$C_{60}$ cannot be prepared by the diffusion method. Recrystallization of the (BEDT-TTF)$_2$$I_3$ salt in fullerene solution yields only the neutral (BEDT-TTF)$_2$$C_{60}$ complex and the BEDT-TTF salts free of fullerene.

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Notes and references

† Abbreviations used in the text: bis(ethylenedithio)tetrathiafulvalene (BEDT−TTF); octamethyletetrathiafulvalene (OMTTF); dibenzotetrathiafulvalene (DBTTF), tetramethylenedithiodimethyltetrathiafulvalene (TMDTDM−TTF); 2.2′,6,6′-tetraphenyldipyranilydene (TPDP).

‡ *Crystal data* for **1:** $C_{70}H_8S_8I_3$, M = 1485.94; black hexagons, 0.4 × 0.2 × 0.2 mm, monoclinic, $C2/c$,a = 29.590(2), b = 9.9271(7), c = 17.2881(12) Å, β = 116.7350(10)°, V = 4535.4(5) Å^3, Z = 4, D_c = 2.176 g cm^{-3}. X-ray data were collected at 90 K using a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo−Kα radiation, λ = 0.71073 Å) and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.3° frame−width (ω scan) and 20 s exposure time per frame. The data were integrated, scaled, sorted and averaged using the SMART software package of programs.[10] Empirical absorption corrections were applied (μ = 2.49 mm^{-1}) for the data collected using the SADABS program from the SMART software package.

The structure was solved by direct methods using SHELXTL NT version 5.10.[11] Positions of hydrogen atoms were found from the difference electronic density Fourier synthesis and refined using a 'riding model' with variable U_{iso}; 20392 reflections were collected, 4206 unique (R_{int} = 0.0639). Least-squares refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms gave R_1 = 0.032 [for 3246 observed reflections with $F > 4\sigma(F)$], $wR_2 = 0.085$, final GOF = 1.03.

CCDC 182/1823. See http://www.rsc.org/suppdata/cc/b0/b005541g/ for crystallographic files in .cif format.

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