Synthesis and crystal structure of a C₆₀ complex with a bis(ethylenedithio)tetrathiafulvalene radical cation salt: (BEDT-TTF-I₃)C₆₀

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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): (BEDT-TTF)C₆₀, OMTTF+C₆₀, C₆H₄, and some others. The lack of charge transfer defines the dielectric properties of these complexes. On the other hand, TTF radical cations with different inorganic and organic anions demonstrate metallic and superconducting properties. An example is a series of the BEDT-TTF salts with linear and polymeric anions which possess superconducting properties: (BEDT-TTF)₂X, X = I⁻, Br⁻, AuI₂⁻, ReO₄⁻, Cu(NCS)₂⁻ and (BEDT-TTF)₂H₂O, (BEDT-TTF)₂I⁻, Hal = Cl, Br. 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 (\(\text{C}_60\)).

In previous work we prepared a number of \(\text{C}_60\) 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 (\(\text{D}^+\)I⁻)\(\text{C}_60\), where \(\text{D} = \text{DBTTF}, \text{TPDP}\) or TMDTDM-TTF. 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 cocystallization of BEDT-TTF-I \(_3\) in a saturated fullerene solution in a chlorobenzene–benzonitrile mixture yielded (BEDT-TTF)₂I₂I⁻, which was prepared by slow diffusion of iodine dissolved in acetonitrile which was layered on a solution of \(\text{C}_60\) and BEDT-TTF (1:1) in a 9:1 toluene–1,2-dichlorobenzene mixture. Crystals of \(\text{I}^\text{2}\) were formed as black hexahedrons on the walls of a flask. Simultaneously, planar rhomb-shaped crystals of \(\text{I}^\text{2}\) free of \(\text{C}_60\) crystallize as an admixture.

The technique is based on the insolubility of both the fullerene and the donor radical cation salt D⁺I⁻ 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⁺I⁻)\(\text{C}_60\) compound. Single crystal X-ray diffraction data of \(\text{I}^\text{2}\) shows that \(\text{C}_60\), (BEDT-TTF)⁺, and I⁻ are fully ordered, with the fullerene, (BEDT-TTF)⁺ and I⁻ moieties residing in special positions on two-fold axes. The densely packed \(\text{C}_60\) layers parallel to the bc plane alternate with (BEDT-TTF)⁺, and I⁻ layers. Fig. 1 shows the view of the crystal structure of \(\text{I}^\text{2}\) along the b axis. The shortest distance between the centers of the \(\text{C}_60\) molecules in parallel layers is 15.61 Å. Within the layers each \(\text{C}_60\) molecule is surrounded by six adjacent \(\text{C}_60\) molecules with center-to-center distances equal to 9.93–9.97 Å, close to similar distances in neat \(\text{C}_60\) crystals (9.94 Å at 153 K). Adjacent \(\text{C}_60\) 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 iodon radical ion (Fig. 2) consists of chains in which the (BEDT-TTF)⁺ ion alternates with I⁻. 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 (BEDT-TTF)⁺ and I⁻ within the layer. Short van der Waals S–S contacts (3.80–3.96 Å) link two (BEDT-TTF)⁺ and I⁻ molecules in adjacent chains. The shortest S–S distance between (BEDT-TTF)⁺ and I⁻ 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. 1 The projection of the crystal structure of \(\text{I}^\text{2}\) along the b axis.

Fig. 2 The projection of the layer comprising (BEDT-TTF)⁺ and I⁻ on the bc plane. Only H-atoms involved into short van der Waals contacts with I⁻ are shown.
The ordering of the \( \text{C}_60 \) molecules in \( \text{I} \) allows their bond lengths to be analyzed. The averaged lengths of the 6–6 and 6–5 bonds of \( \text{C}_60 \) are 1.395(5) and 1.449(5) \( \text{Å} \), respectively, the values being close to those of the 6–6 and 6–5 bonds in neutral (BEDT-TTF)\( \text{C}_60 \) [1.389(7) and 1.452(1) \( \text{Å} \), respectively]. The diameters of the \( \text{C}_60 \) 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 \( \text{Å} \), thus the deviation from sphericity is only 0.03 \( \text{Å} \).

Thus, the structure of \( \text{I} \) retains to a great extent the features of the \( \text{C}_60 \) structure, with radical cation layers separating the \( \text{C}_60 \) layers. The (BEDT-TTF)\( ^+ \) and \( \text{I}^− \) ions interact mostly electrostatically within the layer, while they form van der Waals contacts with fullerene layers.

\( \text{I} \) is a semiconductor with \( \sigma = 10^{-4} \text{ S cm}^{-1} \). Such behavior is characteristic of simple BEDT-TTF-\( \text{I}^+ \) salts\(^8 \) 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 \( \pi \)-orbitals of the (BEDT-TTF)\( ^+ \) 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)\( _3\text{I}_2\text{C}_60 \) cannot be prepared by the diffusion method. Recrystallization of the (BEDT-TTF)\( _2\text{I}_2 \) salt in fullerene solution yields only the neutral (BEDT-TTF)\( _2\text{C}_60 \) complex and the BEDT-TTF salts free of fullerene.

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Notes and references

1 Abbreviations used in the text: bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF); octamethyloctatetrafulvalene (OMTTF); dibenzo[tetrafulvalene (DBTTF); tetramethylhexathiomethyltetrafulvalene (TMDTM–TTF); 2,2′,6,6′-tetraphenyldipryridylinylene (TPDP).

2 Crystal data for I:\( \text{C}_6\text{H}_{12}\text{I}_3 \): \( M = 1485.94 \), black hexagons, 0 \( \times \) 0.2 \( \times \) 0.2 \( \text{mm} \), monoclinic, \( c2\text{c} = 29.590(2), b = 9.9271(7), c = 17.2881(2) \text{Å}, \beta = 116.7350(10)\], \( V = 4535.4(5)\text{ Å}^3 \), \( \alpha = 4\), \( D_{\text{c}} = 2.176\text{ g cm}^{-3} \). X-ray data were collected at 90 K using a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo–K\( \alpha \) radiation, \( \lambda = 0.70730\text{ Å} \)) and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.3° frame–width (\( \omega \) scan) and 20 s exposure time per frame. The data were integrated, scaled, sorted and averaged using the SMART software package of programs\(^\text{10} \). Empirical absorption corrections were applied (\( \mu = 2.69\text{ mm}^{-1} \)) for the data collected using the SASCAD program from the SMART software package.

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

CCDC 182/1823. See http://www.rcsb.org/pdb/data/ccb/6b05/s41g/ for crystallographic files in .cif format.


