A New Series of Radical-cation Salts based on Asymmetrical Ethylenedithiodimethyltetrathiafulvalene (EDTDM-TTF). Properties and Crystal Structure of $(EDTDM\text{-}TTF)_2PF_6$

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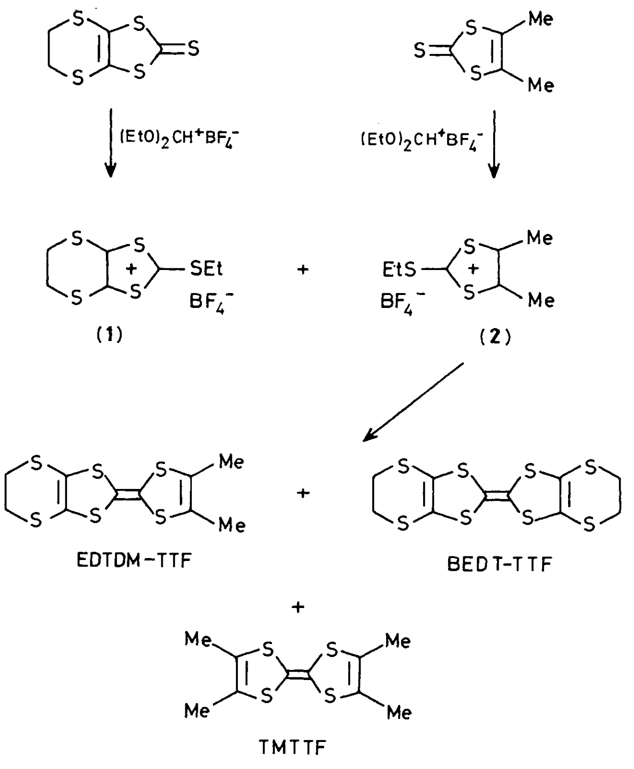
A new series of radical-cation salts with inorganic anions PF_6^-, Br^-, ClO_4^-, $HgCl_3^-$, I^- has been prepared by electrochemical oxidation of ethylenedithiodimethyltetrathiafulvalene (EDTDM-TTF); the electrical conductivity and crystal structure of one of them, $(EDTDM\text{-}TTF)_2PF_6$, are reported and the three-dimensional character of its arrangement is suggested.

Most of the known organic metals consist of planar donor or acceptor molecules and can be considered as quasi-one-dimensional compounds. However, the low-temperature Peierls instability inherent in one-dimensional systems destroys the metal state as in the one-dimensional salts of tetramethyltetrathiafulvalene (TMTTF), $(TMTTF)_2X$, where X = PF_6^-, ClO_4^- and so on, which have metal–insulator transition at low temperature.[1] Metal state stabilization is possible for two- and three-dimensional organic metals where an increase of dimensionality is due to the additional interchain interactions. Such two-dimensional crystal structures with significant transverse intermolecular interactions *via* sulphur atoms are typical for the salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[2] An interest in this donor and its derivatives was enhanced by the recent discovery of superconductivity in some of its salts.[3]

In this paper a new series of radical-cation salts based on the asymmetrical molecule of ethylenedithiodimethyltetrathiafulvalene (EDTDM-TTF) with PF_6^-, Br^-, ClO_4^-, $HgCl_3^-$, I^- anions, and the crystal structure and electrical properties of $(EDTDM\text{-}TTF)_2PF_6$ are presented.

EDTDM-TTF was obtained[4] by cross coupling of the appropriate 2-ethylthio-1,3-dithiolium salts (**1**) and (**2**). The product was purified by chromatography on an Al_2O_3 column (eluant benzene : hexane 1 : 1, R = 0.5) and recrystallized from benzene to give pink–red crystals, m.p. 169—170 °C; u.v.–visible (1,1,2-trichloroethane, nm): 312 (ε 4.07), 340 (4.00), 459 (2.82); i.r. (KBr, cm^{-1}): 768, 900, 1070—1156, 1280, 1425, 1620, 2887. Electrocrystallization at a platinum electrode[5] using constant current (3 μA) at stabilized temperature below 10 °C in a 1,1,2-trichloroethane solution (c 3 × 10^{-3} M) with Bu_4NPF_6, Bu_4NBr, Bu_4NClO_4, Bu_4NHgCl_3, and Bu_4NI_3 as supporting electrolytes (c 0.1 M) yielded single crystals of the respective salts.



Full *X*-ray analysis was carried out for the salt $(EDTDM\text{-}TTF)_2PF_6$; the main crystallographic data are presented in Table 1, along with those for other salts. Crystals of $(EDTDM\text{-}TTF)_2PF_6$ are triclinic, 1065 independent non-zero reflections were obtained on a four-circle *X*-ray RED-4 diffractometer (Cu-K_α radiation). Absorption in the crystal was not considered. The structure was solved by direct methods and refined using a full-matrix anisotropic approximation (isotropic for H atoms)[6] to $R = 0.059$.

The structure of the molecule is shown in Figure 1. Its bond lengths are consistent with the analogous ones in $(TMTTF)_2PF_6$[7] and α-$(BEDT\text{-}TTF)_2PF_6$.[8] The molecular arrangement in the crystal is shown in Figures 2 and 3. The PF_6^- anion is localized on the centre of symmetry and there are stacks of EDTDM-TTF molecules along the *c*-axes (Figure 2). Considerable deviations from planarity of the ethylenedithio-fragment, which adopts the chair conformation, prevent the close-packed arrangement of the molecules in the stack, analogous to the earlier investigated α- and β-$(BEDT\text{-}TTF)_2PF_6$.[8,9] Intermolecular S–S separations in the stacks are nearly equal to the van der Waals distances. In analogy with α-$(BEDT\text{-}TTF)_2PF_6$, the stacks are irregular. Interatomic distances between A and B molecules in the stacks are shown to be significantly shorter (3.66—3.69 Å) than between A and C molecules (3.88 Å). Apparently, these stacks can be considered as consisting of weak dimers A · · · B.

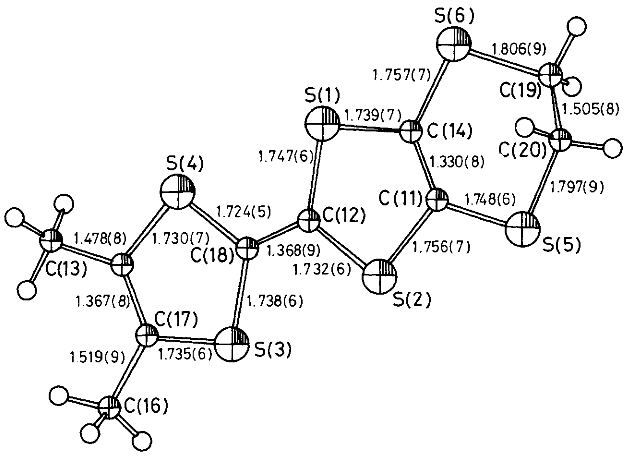


Figure 1. The molecule of EDTDM-TTF. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table 1. Main crystallographic data of radical-cation salts $(EDTDM\text{-}TTF)_2X$, X = PF_6^-, ClO_4^-, Br^-.

	PF_6^-	ClO_4^-	Br^-
a, Å	12.966(3)	27.024(6)	15.412(4)
b, Å	7.814(2)	7.034(2)	17.082(4)
c, Å	7.644(2)	7.850(2)	7.082(4)
α,°	84.576(2)	74.65(2)	
β,°	97.83(2)	87.92(2)	
γ,°	78.84(2)	88.92(2)	99.78(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/b$
M	790.11	744.60	
U, Å^3	747.0(3)	1438.1(6)	1977.6
Z	1	2	
D_c, g cm^{-3}	1.766	1.629	

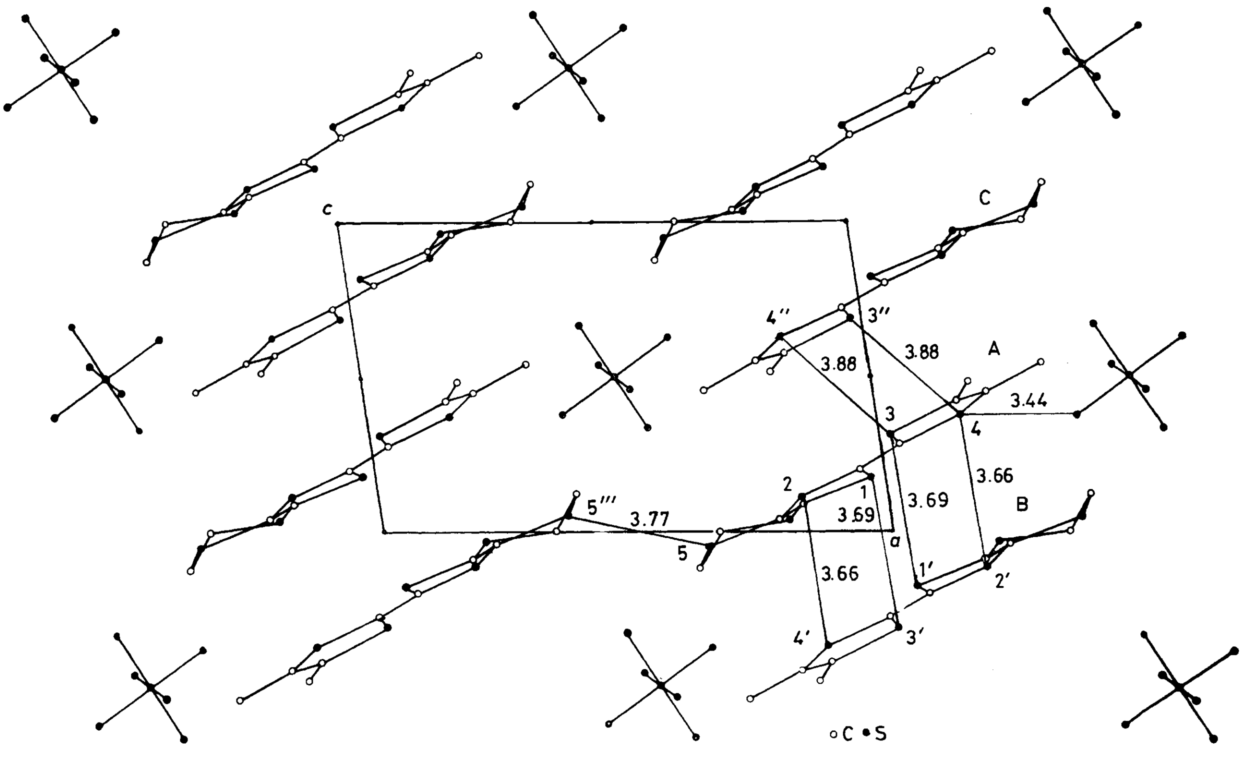


Figure 2. The unit cell of $(EDTDM\text{-}TTF)_2PF_6$ viewed down the *b*-axis.

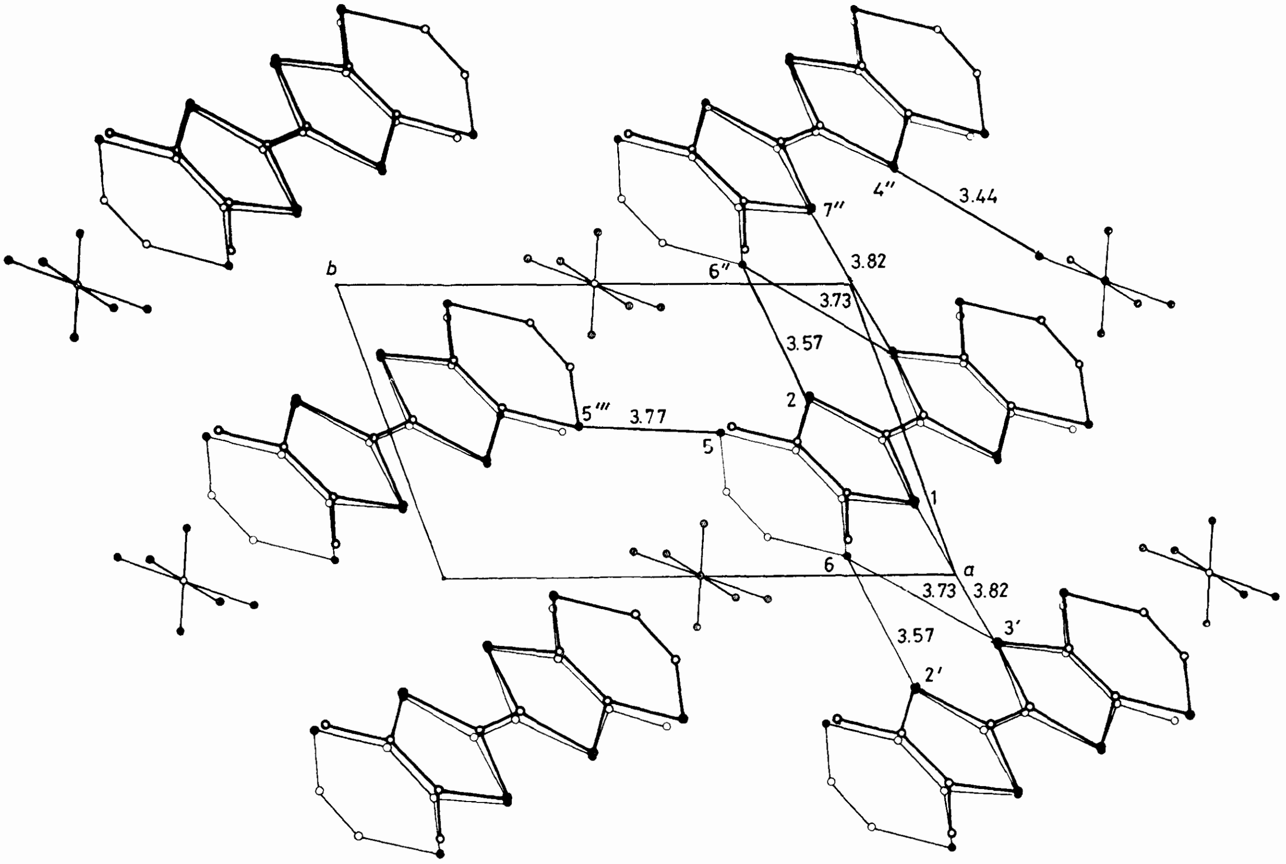


Figure 3. The unit cell of (EDTDM-TTF)$_2$PF$_6$ viewed down the c-axis.

Only the four sulphur atoms of the TTF fragment of the molecule take part in the formation of short contacts in the stack, the non-planar nature of the ethylenedithio-fragment preventing its two sulphur atoms from taking part.

As in the α- and β-(BEDT-TTF)$_2$PF$_6$ crystals the nearest molecules in the neighbouring stacks have short contacts and form an essentially two-dimensional structure. However, the comparison of (BEDT-TTF)$_2$PF$_6$ and the investigated compound shows that the substitution of the ethylenedithio-fragment for two methyl groups leads to a decrease of the number of side-by-side contacts between the donor molecules in the layer. Bulky methyl substituents prevent the transverse approach of the molecules in the layer and cause some mutual displacement of these molecules. Such a displacement of the near-neighbour molecules related by the centre of inversion means there are only two short contacts for each molecule, not four, as in the earlier investigated α- and β-(BEDT-TTF)$_2$PF$_6$. So S(6) (see Figure 3 for numbering) of one ethylenedithio-fragment forms short contacts with S(2′) and S(3′) of the nearest TTF fragment (3.57 and 3.73 Å, respectively), and S(2) and S(3) of the TTF fragment form two short separations with S(6″) of the ethylenedithio-moiety of another neighbouring molecule. Such a relative displacement of the molecules in the layer leads to the decrease of not only the number of side-by-side contacts but also to their noticeable elongation. For instance, in β-(BEDT-TTF)$_2$PF$_6$ the S–S distances lie in the range 3.44—3.52 Å, in α-(BEDT-TTF)$_2$PF$_6$ 3.48—3.61 Å, but in (EDTDM-TTF)$_2$PF$_6$ 3.57—3.73 Å. Apparently, such an arrangement of the molecules in the layer decreases their d_π–d_π interaction and disturbs the two-dimensionality of the crystal structure. It is to be noted, however, that in contrast to the two-dimensional crystal structure of α- and β-(BEDT-TTF)$_2$PF$_6$, in the crystal structure of the investigated compound there is a slightly diminished distance S(5) · · · S(5‴) (3.77 Å) between the near-neighbour molecules of the neighbouring layers separated by PF$_6^-$ anions. Although the shortening is not significant, it apparently allows us to consider this structure to be three-dimensional.

In conclusion, the introduction of asymmetry by the substitution of an ethylenedithio-fragment for two methyl groups leads to some weakening of the two-dimensionality in the crystal in comparison with the analogous salts of BEDT-TTF.

The structure explains the observed conductive properties of the investigated compound. The room-temperature conductivity of single crystals of (EDTDM-TTF)$_2$PF$_6$ with gold contacts σ(300 K) is equal to 3 ohm^{-1} cm^{-1} and falls when the temperature decreases, activation energy E_a 0.099 eV. Below 160 K the rate of conductivity decrease changes and it can be described by the activation law with E_a 0.066 eV. The thermoelectric power increases proportionally with T^{-1} when the temperature decreases with activation energy E_a 0.067 eV. It can be concluded from these data that the investigated compound is either an extrinsic semiconductor whose impurity levels begin to have effect below 160 K, or an intrinsic semiconductor, displaying an increase of the carrier mobility in the low-temperature region.

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