

Synthesis and crystal structure of the new organic conductors (TMTTF)₂(C₆H₂N₃O₈), ET₂(C₆H₂N₃O₈) and ET₂(C₆H₂N₃O₇)(THF) with picrate and styphnate anions

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The following new organic conductors with the anions of styphnic acid (trinitroresorcinol) and picric acid were synthesised: (TMTTF)₂(C₆H₂N₃O₈) **1** (TMTTF is tetramethyltetrathiafulvalene), ET₂(C₆H₂N₃O₈) **2** and ET₂(C₆H₂N₃O₇)(THF) **3** [ET is bis(ethylenedithio)tetrathiafulvalene].

While searching new organic conductors and superconductors among radical cation salts and charge-transfer complexes based on tetrathiafulvalene and its derivatives,¹ one has two opportunities to influence their structure. The first one lies in the modifying of the TTF moiety, and the second one, in the introducing of new anions. Organic anions and their influence on the salt structure and electrophysical properties have not been adequately investigated. Thus, there was declared the preparation of organic radical cation salts, which incorporated such organic anions as fluorine containing moieties,^{2,3} oxalate,⁴ acetate,⁴ maleate,⁴ fumarate,⁴ cyanoforn,^{5,6} penta- or tetracyanoallyl,⁶ hexacyanotrimethylenemethanide,⁶ cyananilate⁷ and tris(dicyanomethylene)cyclopropanediide.^{8,9} There are only a few examples describing salts with NO₂ groups in the structure of their anions [e.g., 2,4,7-trinitro-9-(dicyanomethylene)fluorene^{9,10}].

We synthesised some salts of bis(ethylenedithio)tetrathiafulvalene (ET) and tetramethyltetrathiafulvalene (TMTTF) with the anions of picric and styphnic (trinitroresorcinol) acids¹¹ by electrocrystallization. The compounds prepared have the stoichiometry 2:1 and are semiconductors. Simultaneously and independently of us, the synthesis of a salt with the presumable composition (ET)₂(C₆H₂N₃O₇)₂(H₂O)_x was declared.¹²

The salt (TMTTF)₂(C₆H₂N₃O₈) **1** crystallises as thin black needles of 4–5 mm length from a dichloroethane solution after electrochemical oxidation of TMTTF in the presence of tetraethylammonium trinitroresorcinolate.[†] The crystal structure of salt **1** (Figure 1) is formed by one-dimensional nondimerised stacks of cation radicals (TMTTF)^{+1/2} (Figure 2) and trinitroresorcinol anions (C₆H₂N₃O₈)⁻ disposed one after another along the *b*-axis of the crystal. TMTTF stacks and anions alternate along [101] direction of the unit cell. Each of the donor molecule stacks is

surrounded by the chains of anions on four sides. This ‘chess-like’ mode of cation–anion packing has been earlier observed in the molecular conductor (BETS)₂Bi₂Cl₈,¹⁵ and it is similar to those observed in (TTF)₂[NiS₄C₄H₄]¹⁶ and (TMTSF)₂(azaTCNQ)¹⁷ [BETS is bis(ethylenedithio)tetraselenafulvalene, TTF is tetrathiafulvalene, TMTSF is tetramethyltetraselenafulvalene and TCNQ is 7,7',8,8'-tetracyanoquinodimethane].

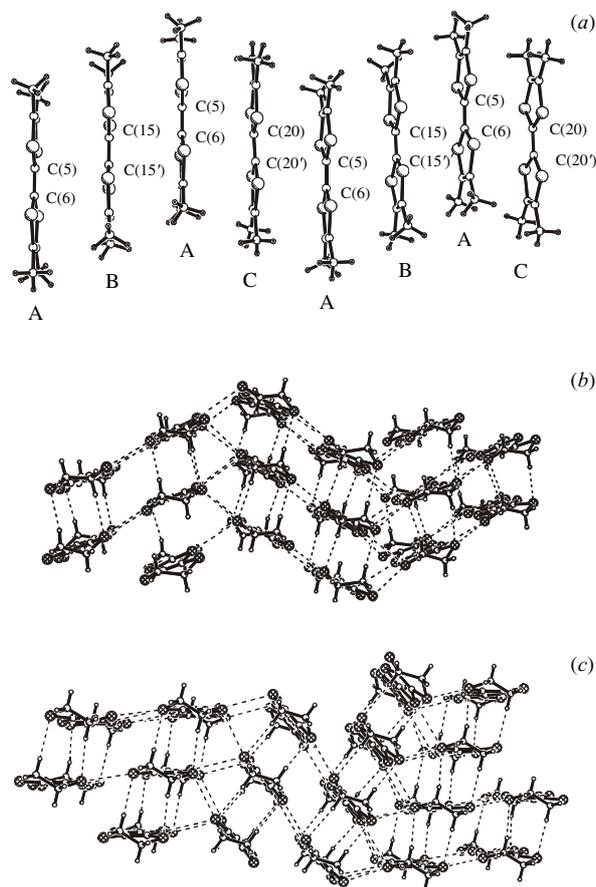


Figure 2 Packing of conducting layers in the (a) **1**, (b) **2** and (c) **3** salts.

[†] Crystal data for **1**: C₂₆H₂₆N₃O₈S₈, *M* = 746.98, monoclinic, space group *P*2₁/*n*, *a* = 12.634(6) Å, *b* = 14.343(7) Å, *c* = 18.550(9) Å, β = 105.95(4)°, *V* = 3232(3) Å³, *Z* = 4, *d*_{calc} = 1.572 g cm⁻³. The experiment was carried out on a KM-4 automated diffractometer (Kuma Diffraction, Poland) with graphite-monochromated MoKα radiation using the ω/2θ scanning technique (6718 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELX-86¹³ and SHELXL-93¹⁴ program packages.

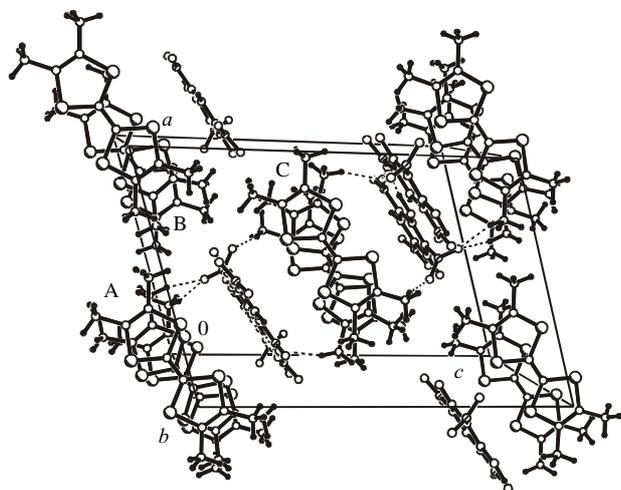


Figure 1 Crystal structure of (TMTTF)₂(C₆H₂N₃O₈) **1**.

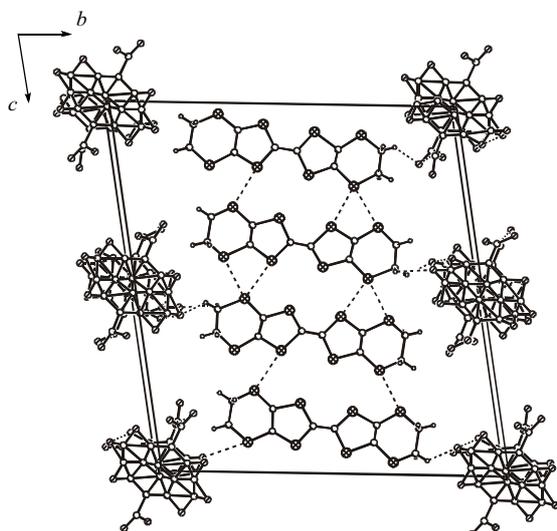


Figure 3 The crystal structure of $\text{ET}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_8)_2$.

TMTTF cation radicals are characterised by different types of symmetry. One of the cation radicals is in the common position and has no local elements of symmetry (cation radical A), and the two others (B and C) are centrosymmetric (Figure 1).

The trinitroresorcinol anions ($\text{C}_6\text{H}_2\text{N}_3\text{O}_8$)⁻ alternate along the *b*-direction of the crystal. One of the NO_2 groups displaces from the benzene ring plane (the dihedral angle between the planes of the central six-membered ring and the NO_2 group is equal to 76.8°). All other atoms of the anion lie in the plane of a benzene moiety. There are no shortened intrastack S...S contacts in TMTTF.

At 300 K, the conductivity of **1** is $\sigma_{300} = 2.1 \times 10^{-3} \text{ S cm}^{-1}$. The temperature dependence of the conductivity has an activation character. Two sections can be recognised corresponding to the two different values of activation energy $E_{A1} = 0.12 \text{ eV}$ (280–400 K) and $E_{A2} = 0.094 \text{ eV}$ (200–280 K). In the phase transition region, the conductivity jumps.

The ET styphnate single crystals of $\text{ET}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_8)_2$ were prepared for ten days by electrochemical oxidation at ambient

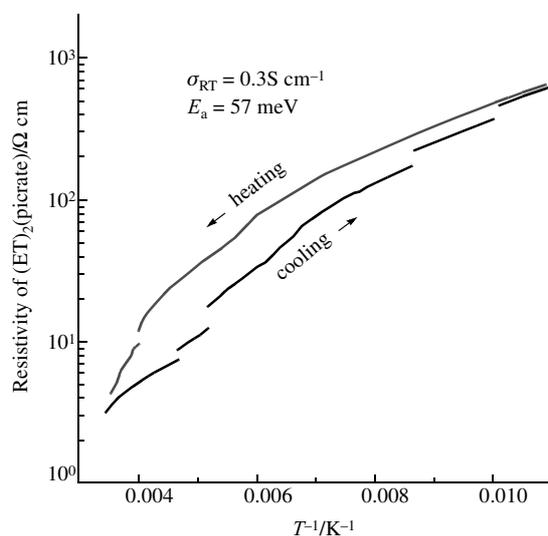


Figure 4 The temperature dependences of conductivity for the single crystal of salt **3**.

‡ *Crystal data for 2*: $\text{C}_{26}\text{H}_{18}\text{N}_3\text{O}_8\text{S}_{16}$, $M = 1013.39$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.422(1) \text{ \AA}$, $b = 21.761(2) \text{ \AA}$, $c = 23.331(2) \text{ \AA}$, $\alpha = 80.96(0)^\circ$, $\beta = 84.44(1)^\circ$, $\gamma = 89.99(1)^\circ$, $V = 4202.5(8) \text{ \AA}^3$, $Z = 4$. The experiment was carried out on a Mac Science DIP-2020K diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation (5615 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXL-93¹⁴ program packages.

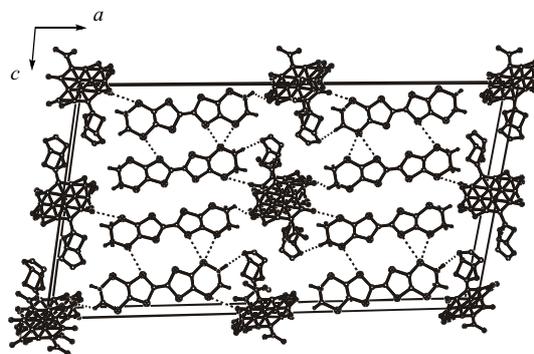


Figure 5 The crystal structure of $\text{ET}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)(\text{THF})_3$.

temperature in a THF solution at $1 \mu\text{A cm}^{-2}$ current density. The conductivity was measured by a d.c. four-probe technique; it has an activation character, $\sigma_{300} = 4.7 \times 10^{-2} \text{ S cm}^{-1}$ and $E_A = 0.097 \text{ eV}$. The crystal structure of salt **2** is presented in Figure 3.

The ET cation radicals form layers (Figure 2) separated by strongly disordered styphnate anions, where one of the NO_2 groups displaces from the benzene-ring plane.

Electrochemical crystallization of ET gave salt $\text{ET}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)(\text{THF})_3$, elemental analysis of which indicated that a molecule of THF was incorporated in this salt. The stoichiometry was found to be 2:1:1.[§]

In complex **3**, the ET molecules form a two-dimensional segregated layer in the *bc*-plane, which is sandwiched by the anion layers. The stacking pattern of the ET molecules is of α'' -type (Figure 2). Picrate anions and THF molecules in the anion layer are orientationally disordered into two sites. This salt shows a semiconductive behaviour (Figure 4). The conductivity has an activation character: $\sigma_{RT} = 0.3 \text{ S cm}^{-1}$, $E_A = 57 \text{ meV}$. The temperature dependence of the magnetic susceptibility of **3** can be expressed by the alternate chain model¹⁸ ($|J| = 143 \text{ K}$, $\alpha = 0.419$) in the range over 100 K. The magnetic susceptibility at room temperature is $8.7 \times 10^{-4} \text{ emu mol}^{-1}$, which is high and comparable to Mott insulators of ET materials. The crystal structure of the salt is presented in Figure 5.

Here, as well as in the two previous salts, one of the nitro groups displaces from the ring plane in contrast to the 1:1 complex of hexanitrostyrene (HNS) with TTF,¹⁹ where all nitro groups lie in the plane of the corresponding benzene rings.

Thus, new conducting salts of TMTTF and ET with picrate and styphnate anions were electrochemically synthesised. The incorporation of organic anions into the structure of radical cation salts of the TTF series can be promising for the synthesis of new conducting materials.

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§ *Crystal data for 3*: $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_8\text{S}_{16}$, $M = 1069.50$, monoclinic, space group $C2/c$ (no. 15), $a = 43.152(3) \text{ \AA}$, $b = 4.2160(3) \text{ \AA}$, $c = 23.256(1) \text{ \AA}$, $\beta = 99.29(0)^\circ$, $V = 4175.44(40) \text{ \AA}^3$, $Z = 4$. The experiment was carried out on a Mac Science DIP-2020K diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation (3464 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXL-93¹⁴ program packages. Atomic coordinates, bond lengths, bond angles and thermal parameters for **1–3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/90.

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