Synthesis and crystal structure of the new organic conductors $(TMTTF)_2(C_6H_2N_3O_8)$, $ET_2(C_6H_2N_3O_8)$ and $ET_2(C_6H_2N_3O_7)(THF)$ 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: $(TMTTF)_2(C_6H_2N_3O_8)$ **1** (TMTTF is tetramethyltetrathiafulvalene), $ET_2(C_6H_2N_3O_8)$ **2** and $ET_2(C_6H_2N_3O_7)(THF)$ **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] cyanoform,[5,6] penta- or tetracyanoallyl,[6] hexacyanotrimethylenemethanide,[6] cyananilate[7] and tris(dicyanomethylene)-cyclopropanediide.[8,9] There are only a few examples describing salts with NO_2 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) acids[11] 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 $(ET)_2(C_6H_2N_3O_7)_2(H_2O)_x$ was declared.[12]

The salt $(TMTTF)_2(C_6H_2N_3O_8)$ **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 trinitroresorcinate.† 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 $(C_6H_2N_3O_8)^-$ 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 $(BETS)_2Bi_2Cl_8$,[15] and it is similar to those observed in $(TTF)_2[NiS_4C_4H_4]$[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].

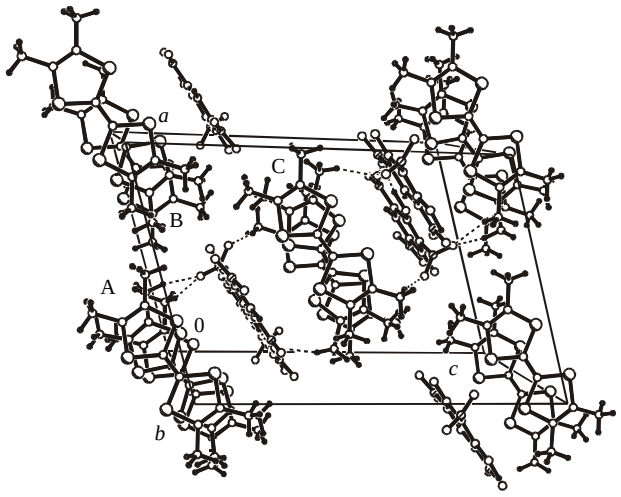

Figure 1 Crystal structure of $(TMTTF)_2(C_6H_2N_3O_8)$ **1**.

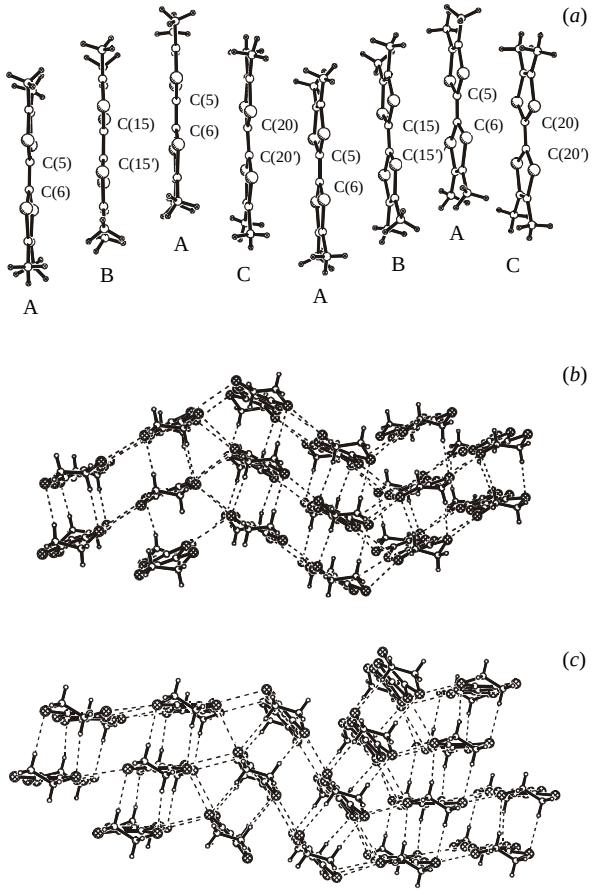

Figure 2 Packing of conducting layers in the (*a*) **1**, (*b*) **2** and (*c*) **3** salts.

† *Crystal data for* **1**: $C_{26}H_{26}N_3O_8S_8$, M = 746.98, monoclinic, space group $P2_1/n$, a = 12.634(6) Å b = 14.343(7) Å, c = 18.550(9) Å, β = 105.95(4)°, V = 3232(3) Å^3, 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 $\omega/2\theta$ scanning technique (6718 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELX-86[13] and SHELXL-93[14] program packages.

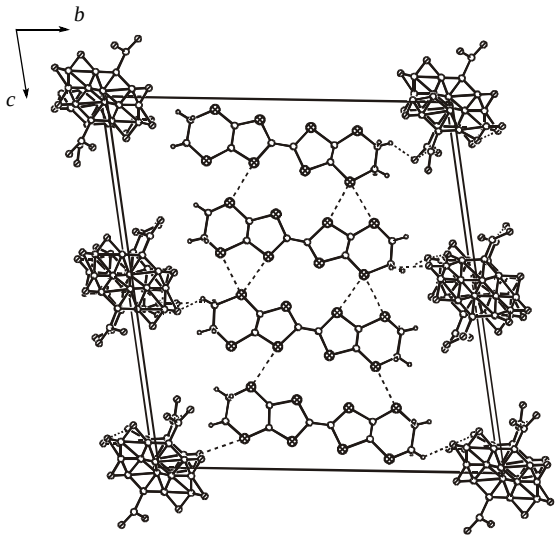

Figure 3 The crystal structure of $ET_2(C_6H_2N_3O_8)$ **2**.

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 $(C_6H_2N_3O_8)^-$ 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 $\sigma_{300} = 2.1\times10^{-3}$ 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 $E_{A1} = 0.12$ eV (280–400 K) and $E_{A2} = 0.094$ eV (200–280 K). In the phase transition region, the conductivity jumps.

The ET styphnate single crystals of $ET_2(C_6H_2N_3O_8)$ **2**‡ were prepared for ten days by electrochemical oxidation at ambient

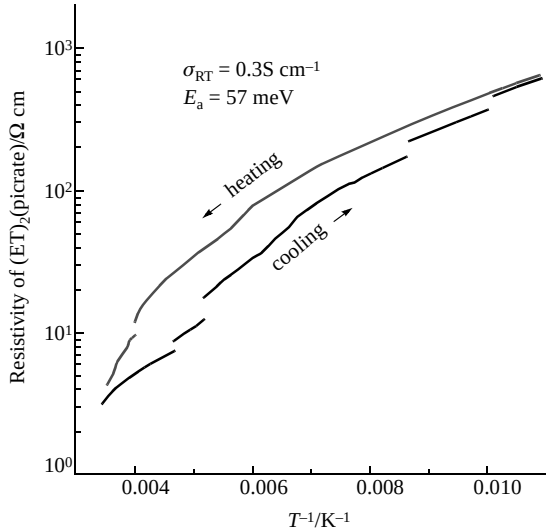

Figure 4 The temperature dependences of conductivity for the single crystal of salt **3**.

‡ *Crystal data for* **2**: $C_{26}H_{18}N_3O_8S_{16}$, $M = 1013.39$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.422(1)$ Å, $b = 21.761(2)$ Å, $c = 23.331(2)$ Å, $\alpha = 80.96(0)°$, $\beta = 84.44(1)°$, $\gamma = 89.99(1)°$, $V = 4202.5(8)$ Å^3, $Z = 4$. The experiment was carried out on a Mac Science DIP-2020K diffractometer with graphite-monochromated MoKα radiation (5615 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXL-93[14] program packages.

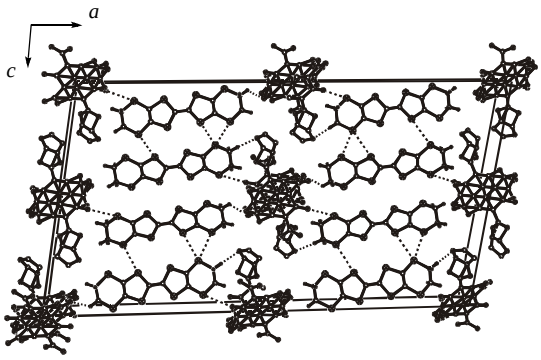

Figure 5 The crystal structure of $ET_2(C_6H_2N_3O_7)(THF)$ **3**.

temperature in a THF solution at 1 μA cm^{-2} current density. The conductivity was measured by a d.c. four-probe technique; it has an activation character, $\sigma_{300} = 4.7\times10^{-2}$ S cm^{-1} and $E_A = 0.097$ 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 $ET_2(C_6H_2N_3O_7)$-(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: $\sigma_{RT} = 0.3$ S cm^{-1}, $E_A = 57$ meV. The temperature dependence of the magnetic susceptibility of **3** can be expressed by the alternate chain model[18] ($|J| = 143$ K, $\alpha = 0.419$) in the range over 100 K. The magnetic susceptibility at room temperature is 8.7×10^{-4} 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 hexanitrostylbene (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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References

1 T. Ishiguro, K. Yamaji and G. Saito, *Organic Superconductors*, 2nd edn., Springer, Berlin, 1998.

2 U. Geiser, J. A. Schlueter, H. H. Wang, A. M. Kini, J. M. Williams, P. P. Sche, H. L. Zakowicz, M. L. VanZile and J. D. Dudek, *J. Am. Chem. Soc.*, 1996, **118**, 9996.

§ *Crystal data for* **3**: $C_{30}H_{26}N_3O_8S_{16}$, $M = 1069.50$, monoclinic, space group $C2/c$ (no. 15), $a = 43.152(3)$ Å, $b = 4.2160(3)$ Å, $c = 23.256(1)$ Å, $\beta = 99.29(0)°$, $V = 4175.44(40)$ Å^3, $Z = 4$. The experiment was carried out on a Mac Science DIP-2020K diffractometer with graphite-monochromated MoKα radiation (3464 reflections). The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXL-93[14] 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.

3 H. H. Wang, U. Geiser, M. E. Kelly, M. L. VanZile, A. J. Skulan, J. M. Williams, J. A. Schlueter, A. M. Kini and S. A. Sirchio, *Mol. Cryst. Liq. Cryst*., 1996, **284**, 427.
4 P. Kathirgamanathan, S. A. Mucklejohn and D. R. Rosseinsky, *J. Chem. Soc., Chem. Commun*., 1979, 86.
5 M. A. Beno, H. H. Wang, L. Soderholm, K. D. Carlson, L. N. Hall, L. Nunez, H. Rummens, B. Andersen, J. A. Schluter, J. M. Williams, M.-H. Whangbo and M. Evain, *Inorg. Chem*., 1989, **28**, 150.
6 (*a*) H. Yamochi, T. Tsuji, G. Saito, T. Suzuki, T. Miyashi and C. Kabuto, *Synth. Met*., 1988, **27**, A479; (*b*) H. Yamochi, C. Tada, S. Sekizaki, G. Saito, M. Kusunoki and K. Sakaguchi, *Mol. Cryst. Liq. Cryst*., 1996, **284**, 379.
7 Md. B. Zaman, Y. Morita, J. Toyoda, H. Yamochi, G. Saito, N. Yoneyama, T. Enoki and K. Nakasuji, *Chem. Lett*., 1997, 729.
8 T. Fukunaga, M. D. Gordon and P. J. Krusic, *J. Am. Chem. Soc*., 1976, **98**, 611.
9 S. Horiuchi, H. Yamochi, G. Saito, K. Sakaguchi and M. Kusunoki, *J. Am. Chem. Soc*., 1996, **118**, 8064.
10 O. Drozdova, H. Yamochi, K. Yakushi, M. Uruichi, S. Horiuchi and G. Saito, *Proceedings of the Synth. Met. ICSM 2000*, Austria, 2000.
11 G. G. Abashev, E. V. Shklyaeva and A. G. Tenishev, *ISCOM-99*, Oxford, 1999, p. 5.
12 C. Rodrigues, E. V. Lopes, M. Almeida and R. T. Henriques, *ISCOM-99*, Oxford, 1999, p. 108.
13 G. M. Sheldrick, *SHELX 86, Program for Crystal Structure Determination*, University of Göttingen, Germany, 1986.
14 G. M. Sheldrick, *SHELXL 93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1993.
15 N. D. Kushch, O. A. Dyachenko, V. V. Gritsenko, P. Cassoux, C. Faulman, A. Kobayashi and H. Kobayashi, *J. Chem. Soc., Dalton Trans*., 1998, 683.
16 P. Cassoux, L. Interrante and J. Kasper, *Mol. Cryst. Liq. Cryst*., 1982, **81**, 293.
17 H. Urayama, T. Inabe, T. Mori, Y. Maruyama and G. Saito, *Bull. Chem. Soc. Jpn*., 1988, **61**, 1831.
18 J. W. Hall, W. E. Marsh, R. R. Weller and W. E. Hatfield, *Inorg. Chem*., 1981, **20**, 1033.
19 M. Fourmigue, K. Boubekeur, P. Batail, J. Renouard and G. Jacob, *New J. Chem*., 1998, 845.

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