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New organic metal β-$(DOET)_2FSO_3 \cdot H_2O$: synthesis and crystal structure

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An organic metal β-$(DOET)_2FSO_3 \cdot H_2O$ based on a novel donor DOET (DOET is (1,4-dioxane-2,3-diyldithio)ethylenedithiotetrathiafulvalene) was synthesized and structurally characterized. Single crystals were prepared by electrochemical oxidation of DOET in the d.c. mode. The salt has a layered structure with the $DOET^{1/2+}$ radical cation layers parallel to the *ab* plane. The FSO_3^- anion is equiprobably disordered over two positions relative to the center of symmetry (1/2, 0, 0). The temperature behavior of conductivity is characteristic of metals in the temperature range from 293 down to 96 K; below 96 K, an increase in resistance is observed.

Key words: organic metals, DOET, electrochemical oxidation, disorder, metal—dielectric transition.

There is only a few studies on radical-cation salts based on a novel donor (1,4-dioxane-2,3-diyldithio)ethylenedithiotetrathiafulvalene (DOET) reported to date. This is due to poor availability of the unsymmetrical donor DOET and complexity of the interpretation of the structures of the DOET-based salts, most of which contain disordered anions and solvated molecules.[1] Radical-cation DOET-based salts show a new type of packing of the radical cation layer[2] while the salts based on a DOET analog (1,4-dioxane-2,3-diyldithio)ethylenedioxytetrathiafulvalene (DOEO) exhibit a rare type of electronic instability and a metallic state stable down to helium temperatures.[3] X-Ray diffraction experiments serve as basis for further quantum chemical calculations of the electronic structure and for construction of theoretical Fermi surfaces of organic metals.[4]

In this work we report on the synthesis, crystal structure, and conductivity of a novel organic metal β-$(DOET)_2FSO_3 \cdot H_2O$ (**1**) based on the DOET and a small tetrahedral anion FSO_3^-.

Results and Discussion

Salt **1** has a layered structure in which the radical-cation layers formed by $DOET^{1/2+}$ units are parallel to the *ab* plane. Island-type FSO_3^- anions are located within channels passing along the *a* axis between the radical cation layers and separated by the translation distance *b* (Fig. 1). The anion is equiprobably disordered over two positions relative to the center of symmetry (1/2, 0, 0) and has a tetrahedral structure with the S—O and S—F bond lengths of 1.417(8)—1.467(5) and 1.609(5) Å, respectively.

Analysis of the difference Fourier electron density syntheses showed that, in addition to the peak of the anion disordered over two positions, there is yet another peak of height 1.76 in the vicinity of the center of symmetry (0, 0, 0). By analogy with the salt $(DOEO)_2HSeO_4 \cdot H_2O$ [3] it was assumed that the anion sublattice contains a water molecule. However, in this case the shortened O...O and O...F distances (1.330 and 1.415 Å, respectively) between the water molecule and the anion demonstrate that the model is rather incomplete. At the moment it is impossible to unambiguously relate the peak to coordinates of a solvent atom or the anion. Exact determination of the structure of the anionic fragment requires additional (including low-temperature) studies.

The structure of **1** contains one independent radical cation $DOET^{1/2+}$ bearing an average formal charge of +0.5 e (Fig. 2). The average deviation from the plane of the S(1)—S(8) and C(1)—C(6) atoms, which form the planar fragment of the $DOET^{1/2+}$ radical cation, is 0.04 Å. The dioxane ring in the $DOET^{1/2+}$ (the C(9), C(10), C(11), C(12), O(9), and O(10) atoms) adopts a chair conformation, being located nearly perpendicular to the planar fragment of the radical cation. The C(7) and C(8) atoms of the ethylene unit also significantly deviate from the average plane (by −0.192(4) and 0.523(4) Å, respec-

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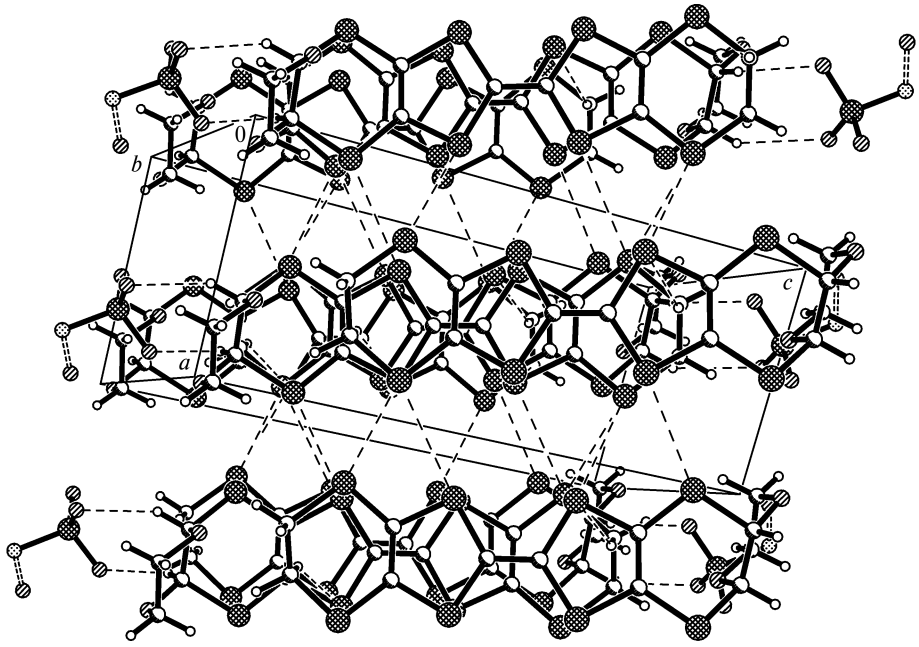

Fig. 1. Crystal structure of β-$(DOET)_2FSO_3 \cdot H_2O$ (**1**). Dashed lines denote the shortened intermolecular distances and double dashed lines denote the O...O distances corresponding to hydrogen bonds.

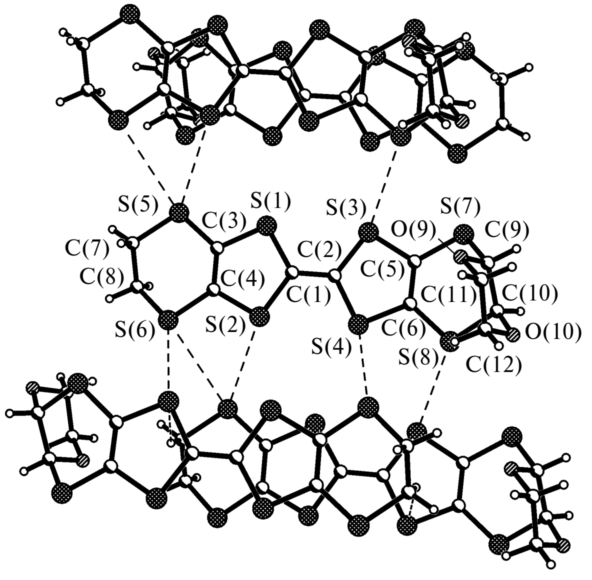

Fig. 2. Atomic numbering scheme for the $DOET^{1/2+}$ radical cation and its environment within the layer in structure **1**. Dashed lines denote the S...S contacts.

tively). Mutual arrangement of the C(9)—C(10) and C(11)—C(12) ethylene units corresponds to eclipsed conformation.

The radical cation layers contain non-equidistant $DOET^{1/2+}$ stacks along the *b* axis, which are formed by centrally symmetrical $(DOET)_2{}^+$ dimers comprising "head-to-tail" arranged $DOET^{1/2+}$ fragments. The distances between the $DOET^{1/2+}$ average planes passing through the C(1)—C(6) and S(1)—S(8) atoms involved in the conjugation system are 3.54(4) Å for the dimer and 3.75(3) Å between the dimers.

Radical cations are stacked without displacement along the short molecular axis. Within the $(DOET)_2{}^+$ dimers, radical cations are shifted along the long axis of $DOET^{1/2+}$ by about the length of the central C=C bond (~1.37 Å). Owing to steric effects of the dioxane rings the shift between dimers is appreciably increased to about 3.84 Å. The structure of the radical cation layer corresponds to the β-type of rational nomenclature[5] (see Fig. 1).

Within the organic layer, radical cations form shortened van der Waals contacts S...S (<3.65 Å), which is characteristic of this class of conducting salts.[4] A total of eight contacts are formed, six $S_{in}...S_{ex}$ and two $S_{ex}...S_{ex}$ contacts (S_{in} are the inner atoms S(1)—S(4) and S_{ex} are the outer atoms S(5)—S(8)) (see Fig. 2). No shortened S...S contacts were found within stacks; they are formed only between stacks along the [100] and $[2\bar{1}0]$ directions.

Salt **1** is an organic metal. As the temperature decreases from room temperature to 96 K, the resistance of a single crystal of **1** decreases by a factor of 2.5; further cooling to the boiling point of liquid helium (4.2 K) causes an increase in the resistance by a factor of 6 relative to the room-temperature value.

An earlier study[2] of DOET-based salts revealed both metallic salts characterized by a metal—dielectric transition and metals stable down to helium temperatures. The conductivity behavior of salt **1** indicates that the compound occupies an intermediate position between these two cases.

Thus, DOET-based salts show a rather wide range of changes in the conducting properties, which makes them quite interesting for physical measurements. In some cases thorough analysis of the structure of the salts obtained makes it possible to establish correlations between the conductivity and crystal structure.

Experimental

Synthesis of β-(DOET)$_2$FSO$_3$•H$_2$O (1). Single crystals of compound **1** were prepared by electrochemical oxidation of DOET in the d.c. mode.[6] DOET (11 mg, 25 mmol) was placed in one leg of a U-shaped electrochemical cell with a porous glass membrane and electrolyte (Bu$_4$NSO$_3$F, 50 mg, 146 μmol) was placed in the other leg. The cell was evacuated to a pressure of ~10^{-2} Torr for several hours, filled with argon, and electrolyte was dissolved in chlorobenzene (20 mL) in argon stream with an additive of anhydrous EtOH (1 mL). Then half the volume of the solution was transferred under argon pressure to the leg filled with the donor and the donor was dissolved with stirring on slight heating. Pt-Electrodes were attached to the cell and the system was sealed and placed in a thermostatted cabinet at 20 °C. Electrochemical oxidation was carried out at an anodic current density of ~0.5 μA cm^{-2} and a voltage varied between 0.5 and 0.7 V.

Conductivity measurements for salt 1. The conductivity was measured by conventional four-probe technique on an automated setup. The room-temperature conductivity in the *ab* plane was 0.3 Ohm^{-1} cm^{-1}. Samples were slowly cooled from room temperature to the boiling point of liquid helium (4.2 K) at a rate of about 1 K min^{-1}.

X-Ray structural study of salt 1. Crystals of $C_{24}H_{22}FO_8S_{17}$ are triclinic; M = 1002.55(3), a = 6.536(1) Å, b = 9.085(2) Å, c = 16.495(2) Å, α = 83.04(2)°, β = 84.42(1)°, γ = 69.58(2)°, V = 909.6(3) Å^3, Z = 1, space group $P\bar{1}$, d_{calc} = 1.830 g cm^{-3}, and μ(Mo) = 1.060 mm^{-1}. The X-ray reflections were collected on an automated KUMA DIFFRACTION KM-4 diffractometer (Mo-Kα-radiation, ω/2θ scan technique, 2.40° < θ < 24.97°). The structure was solved by the direct method using the SHELXS97 program.[7] The positions of hydrogen atoms in DOET$^{1/2+}$ were calculated geometrically and refined isotropically using the riding model. The non-hydrogen atoms were refined anisotropically by the least-squares method using the SHELXL97 program.[8] The final R-factors were as follows: $R_1 = 0.0337$, $wR_2 = 0.0928$ for 2851 reflections with $F^2 > 2\sigma(F^2)$; $R_1 = 0.0372$, $wR_2 = 0.0953$ for a total of 3156 independent reflections; GOOF = 1.083. The residual electron density in the zero Fourier synthesis was $-0.313 < \Delta\rho < 0.481$ e Å^{-3}. Calculations and data processing were performed using the WinGX program package and the ORTEP program.[9,10]

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