

Quasi-two-dimensional organic metals with differently oriented conducting layers

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New layered organic conductors based on selenium- and sulfur-containing donor molecules of bis(ethylenedithio)tetraselenafulvalene (BETS) and deuterated bis(ethylenedithio)-tetrathiafulvalene (ET) with tetrahedral anions of divalent metals of the general formula $(\text{BETS})_4\text{HgBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$, $(\text{ET-d}_8)_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ and $(\text{ET-d}_8)_4\text{HgBr}_4(\text{C}_6\text{H}_5\text{X})$ (where $\text{X} = \text{Cl}, \text{Br}$) were synthesized using halobenzenes as solvents. The crystal structure of $(\text{BETS})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ was studied at room temperature. A distinctive feature of the crystal structures of the compounds is the alternation of the conducting layers, which differ in direction of the radical cation stacks. The conductivity along the layers is of metallic character with the temperature decrease down to 4.3 K for $(\text{BETS})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ and down to 40–105 K for ET-d₈-based compounds, while in the direction perpendicular to the conducting layers the conductivity is semiconducting. A comparative analysis of the temperature dependence of the resistivity for the compounds $(\text{ET})_4\text{HgBr}_4(\text{Solvent})$ (Solvent is 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$, $\text{C}_6\text{H}_5\text{X}$), which are based on ET and its deuterated analog, allows one to suggest that the metal–metal phase transitions observed in the 220–285 K range are of different origin: in the compounds containing 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ they are due to the ordering of solvent molecules, whereas in the compounds containing $\text{C}_6\text{H}_5\text{X}$ the transitions are associated with rearrangements of the terminal ethylene groups.

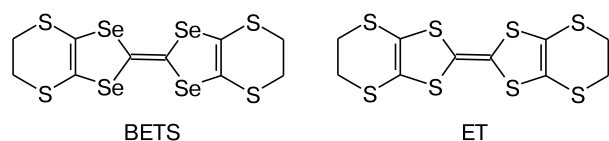
Key words: molecular conductors based on radical cation salts, electrical conductivity, crystal structure, phase transitions.

Compounds of the tetrathiafulvalene family have electron-donor properties and can form stable radical cations. Many radical cation salts with quasi-one-dimensional or quasi-two-dimensional electrical conductivity of the metallic type were synthesized from these compounds.^{1,2} Quasi-two-dimensional organic conductors based on radical cation salts are built of alternating conducting layers of radical cations and non-conducting anionic layers. As a rule, conducting layers consist of stacks of radical cations with the same orientation. However, among the radical cation salts with the stack structure of the conducting layer, there are several compounds with different directions of the stacks in adjacent conducting layers: these are superconductors $\beta''\text{-(ET)}_4(\text{H}_3\text{O})\text{M}(\text{ox})_3(\text{PhCN})$ (see Ref. 3) and conductors with the metal–insulator transition at 150–180 K of the composition $\alpha\text{-}\beta''\text{-(ET)}_4\text{NH}_4\text{M}(\text{ox})_3\text{-(Guest)}$ (see Ref. 4) and $\beta'\text{-}\theta\text{-(ET)}_2[\text{C}(\text{SO}_2\text{CF}_3)_3]$ (see Ref. 5), as well as semiconductors $(\text{EDT-TTF})_3\text{Hg}_2\text{Br}_6$ and $(\text{TMBEDT-TTF})_5\text{Hg}(\text{SCN})_{4-x}\text{I}_x$ (see Ref. 6) and $(\text{TMTSF})_3[\text{Yttrium}(\text{NO}_3)_5]_2(\text{PhCl})$ (see Ref. 7) (ET is bis(ethylenedithio)tetrathiafulvalene, EDT-TTF is ethylenedithiotetrathiafulvalene, TMBEDT-TTF is bis(dimethylethylenedithio)tetrathiafulvalene, and TMTSF is

tetramethyltetraselenafulvalene). In the case where the conducting layers in the conductors with differently oriented layers somewhat differ in structure, the electronic structures of adjacent layers and electron interactions in them can be different, which can result in the formation of subsystems with different properties within the same object.

We have earlier synthesized quasi-two-dimensional organic metals $(\text{BETS})_4\text{MBr}_4(\text{PhX})$ ($\text{M} = \text{Hg}, \text{Cd}$, $\text{X} = \text{Cl}, \text{Br}$) based on BETS (electron-donor selenium-containing compound) with differently oriented conducting layers^{8,9} and with different structures at temperatures below 240 K.¹⁰ Quasi-two-dimensional organic conductors with differently oriented conducting layers with two-charge anions of the tetrahedral geometry $(\text{ET})_4\text{MBr}_4(\text{Solvent})$ were synthesized^{11,12} on the basis of ET, sulfur-containing tetrathiafulvalene. A specific feature of these conductors is different character of conductivity: metallic in the conducting layers and semiconducting perpendicular to these layers, while the qualitatively different character of conductivity for compounds based on BETS and $(\text{ET})_4\text{MBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$ ($\text{M} = \text{Hg}^{11}, \text{Co}^{12}, \text{Cd}^{11}$) is observed in the wide temperature range 300–4.3 K.

Scheme 1



In this work, we synthesized and studied new quasi-two-dimensional organic metals with differently oriented conducting layers (BETS)₄HgBr₄(1,2-C₆H₄Cl₂) (**1**), as well as (ET-d₈)₄HgBr₄(1,2-C₆H₄Cl₂) (**2**) and (ET-d₈)₄-HgBr₄(PhX), where X = Cl (**3**) and Br (**4**), based on deuterated ET. A relationship between the properties and structure of these layered organic conductors is considered.

Results and Discussion

Compounds **1–4** containing electron-donor molecules with the volume larger than that of ET, namely, BETS and ET-d₈, were synthesized and studied. It was assumed that the use of deuterated ET would weaken the interaction between the conducting and anionic layers in the structure of the layered conductor, which can affect the behavior of the resistance and phase transitions.

Compounds **1–4** were synthesized as single crystals by the electrochemical oxidation of BETS or ET-d₈ in the presence of electrolyte [Bu₄N]₂HgBr₄ in the corresponding aromatic solvent, 1,2-C₆H₄Cl₂ or PhX, containing 8–10 vol.% EtOH (Table 1).

The crystal structure of **1** was determined by X-ray diffraction analysis at 297 K, being of tetragonal crystal system. The unit cell parameters are presented in Table 2. The independent part of the crystal structure (Fig. 1) includes half a radical cation of BETS, which is situated near the inversion center (designated by letter **B** in Fig. 1) and half a radical cation situated near the 2-fold axis (designated by letter **A** in Fig. 1), the fourth part of the anion [HgBr₄]^{2–} (with Hg atoms lying in the axis -4 and Br atoms in the general position), and the solvent (dichloro-

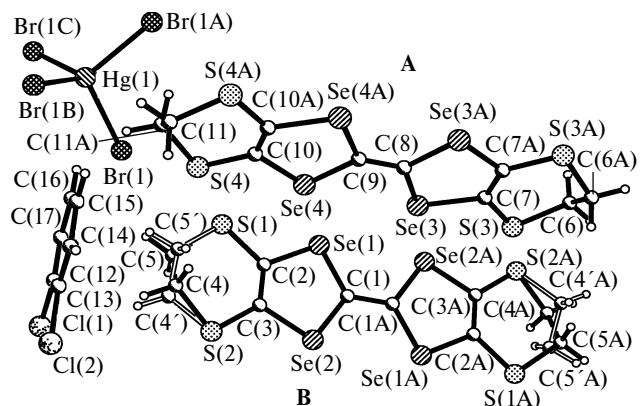


Fig. 1. Fragment of the crystal structure of compound **1** according to the X-ray diffraction data.

benzene) molecule disordered by the axis -4 . The disordering of the terminal CH₂ fragments over two positions with occupancies of 0.65 and 0.35 was revealed in one of the organic radical cations (see Fig. 1).

The unit cell consists of four conducting radical cation layers of the same structure separated by anionic layers in which solvent molecules are present together with discrete anions [HgBr₄]^{2–} (Fig. 2). In the conducting layers (Fig. 3) the radical cations BETS are packed in stacks **A** and **B** of different structures (the so-called θ -type of packing¹³). Each stack consists of independent radicals **A** or **B**, and the dihedral angle between the radical cations from the adjacent stacks is 74.4°. The anionic layer consists of anions [HgBr₄]^{2–} arranged in rows parallel to stacks **A** and solvent molecules (C₆H₄Cl₂) situated near stacks **B**. The angle between the direction of stacks in the adjacent layers is 90°. The formation of this structure can be explained by the influence of the two-charge anions [HgBr₄]^{2–} of tetrahedral geometry forming shortened contacts Br...H with the radical cations of the adjacent layers, which forces the radical cations to pack into stacks running in mutually perpendicular directions. This structure of the conducting layers results in isotropy of the crystal along the directions *a* and *b* of the conducting layer. As a whole, structure of **1** at

Table 1. Conditions for the synthesis and the electrical conductivities at room temperature (σ) of compounds **1–4**^a

Compound	<i>T</i> /°C	Solvent ^{<i>b</i>}	S : Hg : Br : Cl ^{<i>c</i>}	σ	σ _⊥ • 10 ³
				S cm ^{−1}	
(BETS) ₄ HgBr ₄ (1,2-C ₆ H ₄ Cl ₂) (1)	50	1,2-C ₆ H ₄ Cl ₂ —EtOH (11.5 : 1)	16 : 1 : 4 : 2	10	3
(ET-d ₈) ₄ HgBr ₄ (1,2-C ₆ H ₄ Cl ₂) (2)	30	1,2-C ₆ H ₄ Cl ₂ —EtOH (14 : 1)	32 : 1 : 4 : 2	15	1
(ET-d ₈) ₄ HgBr ₄ (PhCl) (3)	30	PhCl—EtOH (14 : 1.5)	32 : 1 : 4 : 1	10	5
(ET-d ₈) ₄ HgBr ₄ (PhBr) (4)	30	PhBr—EtOH (14 : 1.5)	32 : 1 : 5 : 0	20	4

Note. σ_{\parallel} is the conductivity along the layers; σ_{\perp} is the conductivity perpendicular to the layers.

^a Composition of the electrolyte: [Bu₄N]₂HgBr₄ (0.05 mmol), Bu₄NBr (0.002 mmol).

^b The volume ratio of solvents is given in parentheses.

^c According to the electron probe X-ray microanalysis data.

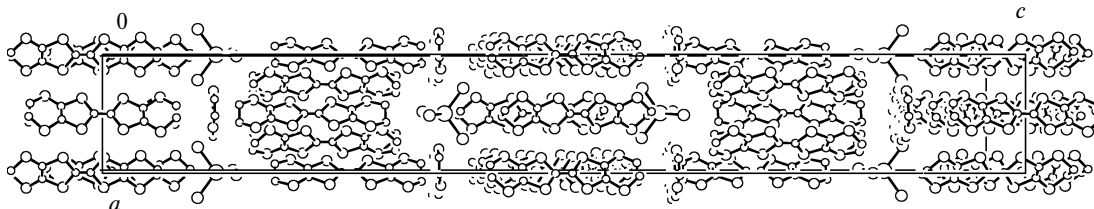


Fig. 2. Projection of the crystal structure of compound **1** on the *ac* plane.

room temperature is analogous to the structures of earlier synthesized $(\text{BETS})_4\text{HgBr}_4(\text{PhCl})$,⁸ $(\text{BETS})_4\text{CdBr}_4(\text{PhBr})$,⁹ and $(\text{ET})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{X}_2)$ ¹¹ ($\text{X} = \text{Cl}, \text{Br}$) at 300 K and to the structure of $(\text{ET})_4\text{CoBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ ¹² at 343 K. Compounds **2–4** have similar crystal lattice parameters at room temperature.

We have previously shown that metal–metal phase transitions are observed in compounds $(\text{Donor})_4\text{MBr}_4(\text{Solvent})$ ($\text{Donor} = \text{BETS}, \text{ET}$).^{8–12} Depending on the number of substituents in halobenzenes, the compounds differ by the behavior of resistivity in the region of phase transition.

In the present work, we studied the electrical conductivity of compounds **1–4**. At room temperature the electrical conductivity of the compounds (σ) is $(10\text{--}20) \text{ S cm}^{-1}$ in the direction parallel to the conducting layers and $(1\text{--}5) \cdot 10^{-3} \text{ S cm}^{-1}$ in the transversal direction (see Table 1).

Table 2. Crystallographic data and the main refinement parameters for compound **1**

Parameter	Value
Molecular formula	$\text{C}_{46}\text{H}_{36}\text{Br}_4\text{Cl}_2\text{HgS}_{16}\text{Se}_{16}$
Molecular weight	2956.20
T/K	293(2)
$\lambda/\text{\AA}$	0.71073
$a/\text{\AA}$	9.7555(14)
$b/\text{\AA}$	9.7555(14)
$c/\text{\AA}$	75.842(15)
α/deg	90
β/deg	90
γ/deg	90
$V/\text{\AA}^3$	7218(2)
Crystal system	Tetragonal
Space group	$I4_1/a$
Z	4
$d_{\text{calc}}/\text{deg cm}^{-3}$	2.720
μ/cm^{-1}	129.89
Scan range, θ/deg	2.10–26.06
Number of experimental/independent reflections (R_{int})	3934/3473 (0.1260)
Number of reflections with $I > 2\sigma(I)$	974
Number of refined parameters	207
Goodness-of-fit	0.952
R_1 for reflections with $I > 2\sigma(I)$	0.0524
wR_2 for all reflections	0.1058

The anisotropy of conductivity in compounds **1–4** is $10^3\text{--}10^4$. The temperature dependence of the longitudinal (R_{\parallel}) and transversal (R_{\perp}) resistivity was studied.

The most interesting results, namely, the metallic character of resistivity along the layers in the whole temperature range and the semiconducting character of resistivity across the layers, were obtained for compound **1** (Fig. 4). In this compound, the resistivity along the layers decreases by 2.5 times as the temperature decreases to 13 K. At $\sim 288 \text{ K}$ the metal–metal phase transition of the I order is observed in compound **1**, due to which the resistivity decreases jumpwise by $\sim 7\%$. In the earlier synthesized conductor $\theta\text{-(ET)}_4\text{CoBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$, the phase transition caused by the structural rearrangement into the triclinic phase with different structures of the conducting layers¹² is accompanied by a similar jumpwise drop of the resistivity. The splitting of single diffraction peaks to several components was observed for $(\text{BETS})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ (**1**) at temperatures below 288 K, indicating the appearance of structural changes. The application of a pressure of 0.3 kbar to crystal **1** rapidly decreases the longitudinal resistivity R_{\parallel} with a temperature decrease (decrease to 5 K results to the decrease in R_{\parallel} by ~ 6 times) but exerts no effect on the phase transition temperature (see Fig. 4). The unusual for organic conductors behavior of the longitudinal and transversal resistivity and the difference in structures of the

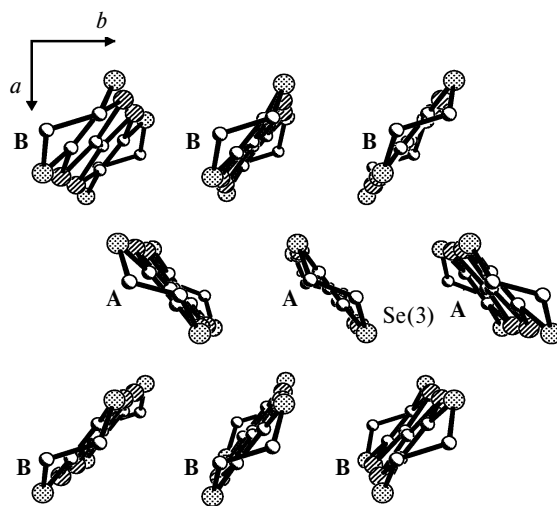


Fig. 3. Structure of the conducting layer in crystal of compound **1**.

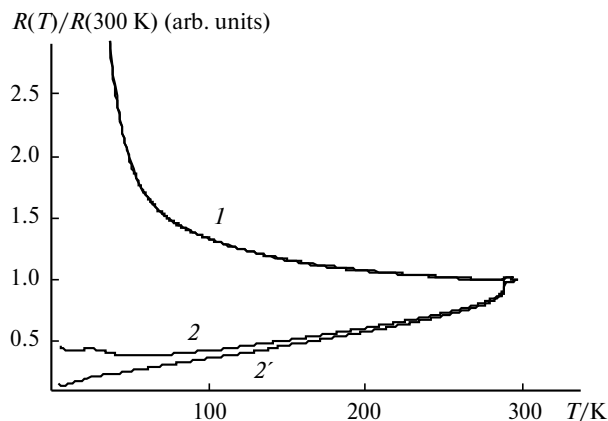


Fig. 4. Temperature dependences of the resistivity in crystals **1** in the direction perpendicular to the conducting layers (*1*) and along the conducting layers before (*2*) and after a pressure of 0.3 kbar was applied to the crystal (*2'*).

adjacent layers of these compounds suggest non-coherent interlayer transport of charge carriers.¹⁴ This makes the synthesized organic conductor a promising object for investigation of the interlayer charge transfer.

It was shown for deuterated compounds **2–4** that with the temperature decrease the resistivity along the layers was metallic down to 40–105 K depending on the solvent, while in the direction perpendicular to the conducting layers the resistivity is semiconducting (see Fig. 5, *a–c*). As the temperature further decreases, resistivity R_{\parallel} increases gradually and at helium temperatures its value is almost

equal to the value observed at 298 K. An increase in R_{\parallel} at temperatures below 50–110 K analogous to that in compounds **3** and **4** (Fig. 5, *d*) is observed in crystals containing undeuterated ET and PhX. However, in the case of the undeuterated analog of compound **2**, a decrease in the longitudinal resistivity R_{\parallel} was detected in the whole temperature range⁴ (Fig. 5, *e*).

Thus, even slight changes in the structure of the electron-donor molecule, such as the replacement of H by D, can result in an increase in the distances between the conducting layer and a decrease in the overlapping of the wave functions of the radical cations and destabilization of the metallic state. A similar effect is observed for the substitution of solvent 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ by 1,2- $\text{C}_6\text{H}_4\text{Br}_2$ in $(\text{ET})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$: the interplanar distances in the radical cation stacks elongate by $\sim 0.013 \text{ \AA}$ only¹¹; however, at temperatures below 60 K resistivity R_{\parallel} increases, at helium temperatures reaching the values close to those observed at room temperatures (see Fig. 5, *e*).

The metal–metal phase transition of the I order occurs in compound **2** at $\sim 284 \text{ K}$, due to which the resistivity decreases jumpwise by $\sim 9\%$. The application of a pressure of 0.3 kbar exerts no effect on the transition temperature (see Fig. 5, *c*). In the undeuterated analog this phase transition is observed at the same temperature (see Fig. 5, *e*). The coincidence of the phase transition temperatures confirms that this transition is due to ordering of solvent molecules.

It is important that the phase transitions have earlier¹¹ been observed in compounds $(\text{ET})_4\text{HgBr}_4(\text{PhX})$ at which

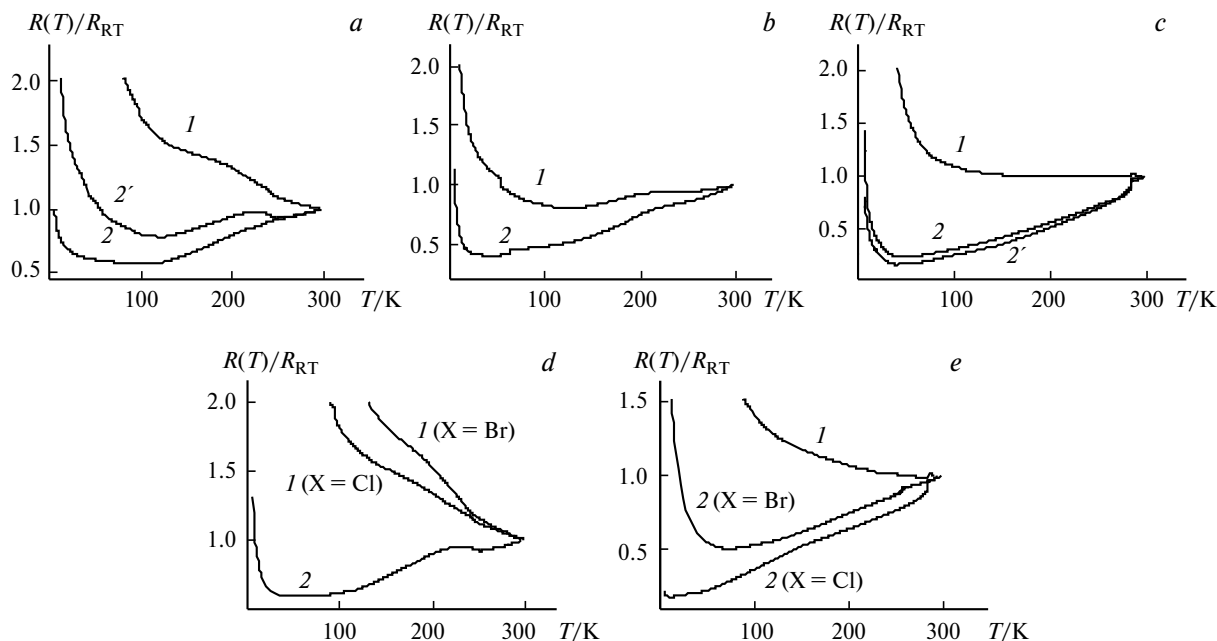


Fig. 5. Temperature dependences of the resistivity in crystals of $(\text{ET-d}_8)_4\text{HgBr}_4(\text{PhCl})$ (*a*), $(\text{ET-d}_8)_4\text{HgBr}_4(\text{PhBr})$ (*b*), $(\text{ET-d}_8)_4\text{HgBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$ (*c*), $\text{ET}_4\text{HgBr}_4(\text{PhX})$ (*d*), and $\text{ET}_4\text{HgBr}_4(1,2\text{-C}_6\text{H}_4\text{X}_2)$ (*e*): *1*, in the direction perpendicular to the conducting layers; *2*, along the conducting layers; *2'*, along the conducting layers at an applied pressure of 0.3 kbar to the crystal.

R_{\parallel} increased gradually (rather than decreased jumpwise) in the temperature range from 230 to 250 K (see Fig. 5, d). In deuterated analogs **3** and **4** we observed no transition in this temperature range when studying the resistivity along the conducting layers (see Fig. 5, a, b). The application of a pressure of 0.3 kbar to crystals of $(d_8\text{-ET})_4\text{HgBr}_4(\text{PhCl})$ recovers this phase transition (see Fig. 5, a). These facts and the extended character of the phase transition suggest that the phase transitions in crystals of $(\text{ET})_4\text{HgBr}_4(\text{PhX})$ ($X = \text{Cl}, \text{Br}$) are related to the conformational rearrangements of the terminal ethylene groups.

Thus, in the present work we synthesized in dichlorobenzene and structurally characterized new quasi-two-dimensional organic metal of the composition $(\text{BETS})_4\text{HgBr}_4(\text{C}_6\text{H}_4\text{Cl}_2)$ with the metallic character of conductivity in the conducting layers and with the semiconducting character perpendicular to the layers with an anisotropy of 10^4 . For this metal, the metal–metal phase transition was observed at 288 K accompanied by a decrease in the resistivity and a change in the crystal lattice parameters.

The comparative study of the temperature dependence of the resistivity of compounds $(\text{ET})_4\text{HgBr}_4(\text{Solvent})$ (Solvent is 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$, PhX ($X = \text{Cl}, \text{Br}$)) based on ET and its deuterated analog suggests that the observed metal–metal phase transitions have different origins: in the compounds containing 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ the transition is due to ordering of the solvent molecule, whereas in the PhX-containing compounds the transition is related to rearrangements of the terminal ethylene groups.

Experimental

X-ray diffraction analysis. The composition and structure of crystals of compound **1** were established by X-ray diffraction analysis. The X-ray diffraction studies of crystals of compound **1** were carried out on a P-4 single-crystal diffractometer (graphite monochromator, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, temperature 297 K, $\theta/2\theta$ scan mode). A low-quality single crystal as a plate $0.35 \times 0.15 \times 0.10 \text{ mm}$ in size was used in experiments. The crystallographic data and the main refinement parameters for compound **1** are given in Table 2.

The crystal structure was solved by a direct method. The positions and temperature parameters of non-hydrogen atoms were refined in the isotropic and then anisotropic approximation by full-matrix least squares. The ordering of the terminal CH_2 fragments over two positions with occupancies of 0.65 and 0.35 was revealed in one of the organic radical cations. Hydrogen atoms were placed in geometrically calculated positions and included in refinement in the riding model. The fragment of the solvate molecule of the solvent (1,2-dichlorobenzene), which is disordered by the axis -4 , was revealed from the difference Fourier syntheses in the crystal structure of compound **1**. The molecule was completed and refined with restraints imposed on the bond lengths in the isotropic approximation with a site occupancy of 0.25, and the positions of the hydrogen atoms for this molecules were not calculated. All calculations were performed using the SHELXTL program package.¹⁵

Electron probe X-ray microanalysis (EPXMA). The composition of crystals of the radical cation salts was determined by the EPXMA method using a CamScan MV 2300 scanning electron microscope equipped with an energy disperse X-ray spectrometer with the semiconducting Si(Li) detector and the INCA Energy 200 software using a 1000-fold magnification and an electron beam energy of 20 keV. The crystals of $(\text{ET})_4\text{Hg}_2\text{Br}_6(\text{PhCl})$, synthesized by a described procedure,¹⁶ were used as a reference.

Conductivity of single crystals was measured by a standard four-contact method at a dc of 10 μA on an automated setup with the temperature decrease from 293 to 4.3 K. Gold contacts (10 μm in diameter) were glued to the crystal using a graphite paste.

Salt $(\text{BETS})_4\text{HgBr}_4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$ (1**)** was synthesized in argon by the electrochemical oxidation of BETS (5 mg, 8.7 mmol) in 13 mL of 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ containing 8% EtOH in the galvanostatic regime at 50 °C and a current strength of 0.4 μA . A mixture of $[\text{NBu}_4]\text{HgBr}_4$ (50 mg, 0.05 mmol) and $[\text{Bu}_4\text{N}]\text{Br}$ (8 mg, 0.0025 mmol) was used as an electrolyte. The crystals as elongated hexagonal plates were obtained within 2–3 weeks.

Bis(ethylenedithio)tetrathiafulvalenium- d_8 tetrabromomercurates(II**) **2–4**** were synthesized by the electrochemical oxidation of ET- d_8 (6 mg, 15 mmol) in 8–10% EtOH in PhX ($X = \text{Cl}, \text{Br}$) or EtOH in 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ at 30 °C and a current strength of 0.15–0.25 μA .

The compositions of compounds **1–4** were determined by the EPXMA method. The conditions of synthesis and the electrical conductivities at room temperature are given in Table 1.

This work was financially supported by the Presidium of the Russian Academy of Sciences (Program for Basic Research No. 21 "Foundations of Basic Research of Nanotechnologies and Nanomaterials") and the Russian Foundation for Basic Research (Project Nos 11-03-01039a and 11-02-00844a).

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Received March 4, 2011