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)tetrathiafulvalene (BETS) and deuterated bis(ethylenedithio)-tetrathiafulvalene (ET) with tetrahedral anions of divalent metals of the general formula (BETS)₄HgBr₄(1,2-C₆H₄Cl₂), (ET-d₈)₄HgBr₄(C₆H₄Cl₂) and (ET-d₈)₄HgBr₄(C₆H₅X) (where X = Cl, Br) were synthesized using halobenzenes as solvents. The crystal structure of (BETS)₄HgBr₄(C₆H₄Cl₂) 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 (BETS)₄HgBr₄(C₆H₄Cl₂) 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 (ET)₄HgBr₄(Solvent) (Solvent is 1,2-C₆H₄Cl₂, C₆H₅X), 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-C₆H₄Cl₂ they are due to the ordering of solvent molecules, whereas in the compounds containing C₆H₅X 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.¹² 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 β″-(ET)₄(H₃O)M(ox)(PhCN) (see Ref. 3) and conductors with the metal—insulator transition at 150—180 K of the composition α-β″-(ET)₄NH₃M(ox)₃-Guest (see Ref. 4) and β″-(ET)₃C(SO₂CF₃)₃] (see Ref. 5), as well as semiconductors (EDT-TTF)₂Hg₂Br₆ and (TMBEDT-TTF)₂Hg(SCN)₃-xIₓ (see Ref. 6) and (TMTSF)₂[Yttrium(NO₃)₃]₂(PhCl) (see Ref. 7) (ET is bis(ethylenedithio)tetrathiafulvalene, EDT-TTF is ethylenedithiotetraphiafulvalene, TMBEDT-TTF is bis(dimethylatedithienothiophene)tetrafulvalene, and TMTSF is tetramethyltetrathiafulvalene). 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 (BETS)₄MBr₄(PPhX) (M = Hg, Cd, X = Cl, Br) based on BETS (electron-donor selenium-containing compound) with differently oriented conducting layers 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 (ET)₄MBr₄(Solvent) were synthesized¹¹ on the basis of ET, sulfur-containing tetra-thiafulvalene. 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 (ET)₄MBr₄-(1,2-C₆H₄Cl₂) (M = Hg¹¹, Co¹², Cd¹¹) is observed in the wide temperature range 300—4.3 K.
In this work, we synthesized and studied new quasi-two-dimensional organic metals with differently oriented conducting layers (BETS)$_4$HgBr$_4$(1,2-C$_6$H$_4$Cl$_2$) (1), as well as (ET-d$_8$)$_4$HgBr$_4$(1,2-C$_6$H$_4$Cl$_2$) (2) and (ET-d$_8$)$_4$HgBr$_4$(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-d$_8$, 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-d$_8$ in the presence of electrolyte [Bu$_4$N]$_2$HgBr$_4$ in the corresponding aromatic solvent, 1,2-C$_6$H$_4$Cl$_2$ 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 [HgBr$_4$]$^{2-}$ (with Hg atoms lying in the axis —4 and Br atoms in the general position), and the solvent (dichlorobenzene) molecule disordered by the axis —4. The disordering 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 (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 [HgBr$_4$]$^{2-}$ (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 packing$^{13}$). 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 dihedral angle between the radical cations from the adjacent layers is 90°. The formation of this structure can be explained by the influence of the two-charge anions [HgBr$_4$]$^{2-}$ 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 | $T/$°C | Solvent$^b$ | S : Hg : Br : Cl$^c$ | $\sigma_{||}$ | $\sigma_{\perp} \times 10^3$ |
|----------|--------|-------------|----------------------|-------------|-----------------|
| (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.* $\sigma_{||}$ is the conductivity along the layers; $\sigma_{\perp}$ is the conductivity perpendicular to the layers.

$^a$ Composition of the electrolyte: [Bu$_4$N]$_2$HgBr$_4$ (0.05 mmol), Bu$_4$NBr (0.002 mmol).

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

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