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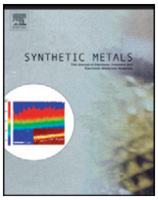

Two-dimensional organic metals θ-$(BETS)_4MBr_4(PhBr)$, M = Cd, Hg with differently oriented conducting layers

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ABSTRACT

New bis(ethylenedithio)tetraselenafulvalene (BETS) based radical cation salts with tetrahedral dianions $[CdBr_4]^{2-}$ and $[HgBr_4]^{2-}$ of the $(BETS)_4MBr_4(PhBr)$ composition were prepared by electrochemical crystallization. Room-temperature crystal structure of $(BETS)_4CdBr_4(PhBr)$ determined by single crystal X-ray diffraction involves BETS radical cation layers of the θ-type packing and insulating layers consisting of $[CdBr_4]^{2-}$ anions and PhBr molecules. In the neighboring conducting layers, the stacks are arranged perpendicular to each other. A metal-to-metal transition within 225–230 K range was found in both $(BETS)_4CdBr_4(PhBr)$ and $(BETS)_4HgBr_4(PhBr)$. The behavior of electrical resistivity of these salts differs substantially along and across conducting layers. The study of magnetoresistance of $(BETS)_4HgBr_4(PhBr)$ revealed weak Shubnikov-de Haas oscillations in fields higher than 6 T.

1. Introduction

Low-dimensional molecular organic conductors form a great family of compounds comprising conducting layers with supramolecular structure and isolating anionic layers. Electron transport properties of organic conductors depend on electronic structure of conducting organic layers, and electronic structure is defined by charge and structure of anionic layers. Small changes in structures of anions can result in essential changes in structures of compounds and their electron transport properties.

Conducting layers of a quasi-two-dimensional metal are usually of the same structure and electron systems in the conducting layers are similar. However, there are compounds, in which conducting layers differ in structure. To our knowledge, several such ion-radical salts have recently been prepared. For example, a radical cation salt based on the unsymmetrical EDOEDT-TTF (4,5-ethylenedioxy-4′,5′-ethylenedithiotetrathiafulvalene) donor molecule of the $(EDOEDT\text{-}TTF)_4Hg_3Br_8$ composition involves $\kappa(4\times4)$- and α''-type layers [1]. The (N-methyl-3,5-diiodopyridinium)$[Ni(dmit)_2]_2$ radical anion salt involves layers one of which is formed by dimerized anion stacks and the other one has a non-columnar structure [2] (dmit = 1,3-dithiole-2-thione-4,5-dithiolate). The α-β″-compounds of $(ET)_4NH_4Fe(ox)_3$(solvent) formula, where solvent is $PhCH(OH)CH_3$ [3], $PhN(CH_3)CHO$, $PhCH_2CN$, $PhCOCH_3$ [4] and ET is bis(3,4;3′,4′-ethylenedithio)-2,2′,5,5′-tetrathiafulvalene, are built of both α and β″ type layers.

X-ray analysis of $(ET)_4NH_4Fe(ox)_3(PhCH(OH)CH_3)$ and (N-methyl-3,5-diiodopyridinium)$[Ni(dmit)_2]_2$ showed that two different conducting layers formed in the same structure were due to the structure of a counter ion layer. In $(ET)_4NH_4Fe(ox)_3(PhCH(OH)CH_3)$, the solvent molecules do not conform to the hexagonal cavities of the anion layer. Therefore, they protrude from the anionic network from the one side only and make two faces of the anion layer non-equivalent that results in different types of ET packing in neighboring conducting layers [3]. In (N-methyl-3,5-diiodopyridinium)$[Ni(dmit)_2]_2$, counter ions are unsymmetrical. As a result, $Ni(dmit)_2$ radical anions are located differently in neighboring conducting layers [2].

Earlier we synthesized a quasi-two-dimensional organic metal, namely, $(BETS)_4HgBr_4(PhCl)$, which involves the two-charged tetrahedral $[HgBr_4]^{2-}$ anion. The salt is characterized by the θ-type packing of the BETS radical cations. It was found experimentally that electron moving inside the layers corresponds to metallic behavior of conductivity, while in the direction perpendicular to the layers it corresponds to a semiconducting type of conductivity [5]. The compound is characterized by high anisotropy of conductivity. As a result of phase transition at $T = 240$–246 K, the structure of conducting layers in $(BETS)_4HgBr_4(PhCl)$ changes. Cationic θ-layers of

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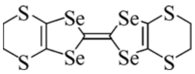
two different types are formed differing in a θ angle value and a number of shortened Se···Se and Se···S contacts between the BETS radical cations. The Fermi surfaces of these non-equivalent crystallographic layers are almost identical. However, the Fermi surfaces are turned approximately by 90° [6]. In compounds showing high anisotropy and such structure, incoherent interlayer transport of carriers is possible since in this case momentum is difficult to be conserved at electron transfer even to a neighboring layer [7]. Such compounds are considered to be promising for the study of interlayer transport of carriers. Therefore, the task was to synthesize compounds with close structures and investigate their electron transport properties in longitudinal and transverse directions.


BETS

In this paper we report on synthesis, temperature variable electrical resistance in longitudinal and transverse directions, and magnetoresistance of new BETS radical cation salts with tetrahedral $[CdBr_4]^{2-}$ and $[HgBr_4]^{2-}$ dianions of the $(BETS)_4CdBr_4(PhBr)$ and $(BETS)_4HgBr_4(PhBr)$ composition together with crystal structure of θ-$(BETS)_4CdBr_4(PhBr)$.

2. Experimental

BETS was synthesized according to the procedure described in [8]. The crystals of the BETS radical cation salts with $[CdBr_4]^{2-}$ and $[HgBr_4]^{2-}$ anions were grown by electrochemical oxidation of BETS at constant current of 0.1–0.2 μA in a H-shaped glass cell on 0.5 mm platinum rod electrode at 49 °C under argon atmosphere.

$(BETS)_4CdBr_4(PhBr)$. The solution of $[Ph_4P]_2CdBr_4$ (55 mg, 0.05 mmol) and $[Ph_4P]Br$ (2 mg, 0.005 mmol) in PhBr/EtOH (8 ml/1.6 ml) was divided equally between the two arms of a H-cell. BETS (5 mg, 0.009 mmol) dissolved in 4.5 ml of PhBr was placed in the anodic chamber, 0.75 ml of PhBr was added in the cathodic one. The crystals of the two types, namely, octagonal plates and truncated octahedrons (14 facets) were collected after 4 weeks. $(BETS)_4CdBr_4(PhCl)$ was prepared in PhCl using a similar procedure.

$(BETS)_4HgBr_4(PhBr)$. The BETS powder (5 mg, 0.09 mmol) was placed in the anodic chamber. The solution of $HgBr_2$ (18 mg, 0.05 mmol) and $[Bu_4N]Br$ (34 mg, 0.1 mmol) in PhBr/EtOH (12 ml/0.5 ml) was divided equally between the two arms of a H-cell. The crystals, which appeared as rectangular plates were collected after 11 days.

Stoichiometry of the crystals was determined by electron probe microanalysis (EPMA). The crystal of $(ET)_4Hg_2Br_6(PhCl)$ was used as a reference compound. EPMA showed S:Cd:Br = 16:1:5 for $(BETS)_4CdBr_4(PhBr)$, S:Hg:Br = 16:1.07:5 for $(BETS)_4HgBr_4(PhBr)$, and S:Cd:Br:Cl = 16:1:4:1 for $(BETS)_4CdBr_4(PhCl)$. The composition of $(BETS)_4CdBr_4(PhBr)$ found by EPMA is in a good agreement with the X-ray data.

Resistance of single crystals was measured by a standard d.c. four-probe technique down to 4.3 K. Platinum wire electrodes of 10 μm in diameter were glued to the crystals with a graphite paste. Magnetoresistance measurements were carried out at 1.4 K and magnetic fields of up to 14.3 T.

X-ray diffraction data for the $(BETS)_4HgBr_4(PhBr)$ single crystal of a truncated octahedron shape were collected at room temperature on a four-circle P-4 automatic diffractometer (BRUKER), λ(Mo Kα) = 0.71073 Å radiation with a graphite monochromator; $\theta/2\theta$ scan). The main crystallographic data for $(BETS)_4HgBr_4(PhBr)$ are: $Br_5C_{46}H_{37}CdS_{16}Se_{16}$, tetragonal, space group $I\ 4_1/a$, $a = 9.764(1)$, $c = 76.03(1)$ Å, $V = 7248.0(16)$ Å^3, $M = 2876.05$, $Z = 4$, $d_{calcd.} = 2.642$ g/cm^3, $F(000) = 5364$; $\mu_{Mo} = 11.590$ mm^{-1}. The unit cell parameters were refined on 35 reflections in the $8° < \theta < 15°$ interval. The 2199 reflections were measured among which 1256 with the intensities $I > 2\sigma(I)$ were used to find a model and refine the structure.

The crystal structure of $(BETS)_4CdBr_4(PhBr)$ was solved by direct methods followed by the Fourier syntheses using the SHELXS-97 (Sheldrick, 1990) program and was refined by SHELXL-97 [9] program to $R = 0.0907$. All non-hydrogen atoms were refined by the full-matrix least-squares method in an anisotropic approximation. The positions of hydrogen atoms were calculated geometrically. It was impossible to localize all positions of C in the PhBr molecule screened by heavy Cd and Br atoms. The positions of two atoms (C and Br) only were revealed from the solvent molecule. CCDC 712740 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing http://data_request@ccdc.cam.ac.uk.

3. Results and discussion

To synthesize the BETS tetrabromocadmates(II) we used $[Ph_4P]_2CdBr_4$ as a supporting electrolyte. Electrochemical oxidation of BETS in PhBr (PhCl) at 49 °C yields $(BETS)_4CdBr_4(PhBr)$ ($(BETS)_4CdBr_4(PhCl)$) as octagonal plates and truncated octahedrons. Both plates and polyhedrons of $(BETS)_4CdBr_4(PhBr)$ formula are characterized by the same temperature variable resistivity. The mixture of $[Bu_4N]Br$ and $HgBr_2$ was used to prepare a Hg-containing compound, $(BETS)_4HgBr_4(PhBr)$. The crystals of only one shape, namely, rectangular plates, were found in this case.

The single crystal X-ray diffraction study of $(BETS)_4CdBr_4(PhBr)$ at room temperature revealed that the crystal consisted of BETS radical cations, $[CdBr_4]^{2-}$ anions, and PhBr molecules. It had a layered structure, in which organic and inorganic layers alternated along the *c* axis.

3.1. Crystal structure of $(BETS)_4CdBr_4(PhBr)$

Crystal structure of $(BETS)_4CdBr_4(PhBr)$ is presented in Fig. 1. The unit cell involves four BETS radical cation layers parallel to the *ab* plane, which are separated by $[CdBr_4]^{2-}$ dianions and PhBr molecules. In each layer, the BETS radical cations form infinite stacks of the θ-type. Each successive radical cation layer can be considered as a previous layer shifted by 1/4 *c* and turned by 90°, i.e. in the neighboring conducting layers, the stacks run in the orthogo-

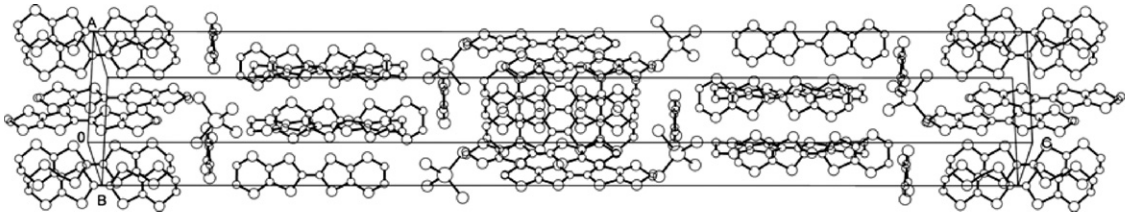


Fig. 1. Crystal structure of θ-$(BETS)_4CdBr_4(PhBr)$. The structure of one unit cell is shown.