First radical cation salts of 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP) with copper(II) metal complex anions: β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ and $(BDA\text{-}TTP)_2CuCl_4$

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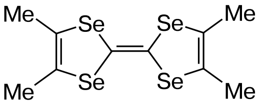
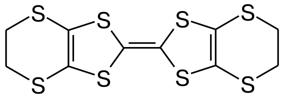
New radical cation salts based on 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP) with copper(II) metal complex anions, β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ and $(BDA\text{-}TTP)_2CuCl_4$, were synthesized and structurally characterized. Single crystals were prepared by electrochemical oxidation of BDA-TTP under galvanostatic conditions. X-ray diffraction study demonstrated that the salts have a layered structure, in which the conducting BDA-TTP layers alternate with the $[Cu_2Cl_6]^{2-}$ or $[CuCl_4]^{2-}$ anions. Both salts show the semiconductor-type temperature dependence of the conductivity.

Key words: synthesis, crystal and electronic structure, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene, radical cation salt, electrochemical oxidation, conductivity, X-ray diffraction study.

In the early 1980s, the discovery of first ambient-pressure organic superconductors based on the radical cation salts tetramethyltetraselenafulvalene (TMTSeF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has spurred the development of chemistry of tetrathiafulvalene (TTF).[1—3]

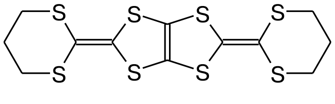


TMTSeF

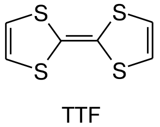


BEDT-TTF

This led to a considerable increase in the number of available radical cation salts based on TTF derivatives, which have a wide spectrum of physical properties, from semiconducting to superconducting.[4,5] However, in spite of vast diversity of available TTF derivatives, the critical superconducting transition temperature (T_c) of their radical cation salts did not rise and remained at about 11.8 K at ambient pressure in all studies, beginning with 1990.[6] In recent years, new approaches have been developed to the design of electron donors for molecular conductors and superconductors based on a decrease in the size of the π-electron system and an expansion of its σ-bonded fragment.[7,8] Recently, a new donor, *viz.*, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP), in which the central TTF fragment is absent, has been synthesized with the use of these approaches.



BDA-TTP



TTF

The BDA-TTP donor forms stable radical cation salts, among which there are ambient-pressure superconductors with T_c = 5.9—7.5 K.[7,8] These superconductors have a layered structure, in which β-type conducting radical cation layers alternate with nonconducting anionic layers.

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However, known radical cation salts BDA-TTP are few in number (about 15) and are limited primarily by salts with singly-charged anions having octahedral (PF_6, SbF_6, and AsF_6) or tetrahedral (ClO_4, BF_4, ReO_4, $FeCl_4$, and $GaCl_4$) geometry.[7,8] For salts of the BEDT-TTF family, the shape and size of the anion have a considerable effect on the character of packing of radical cations and, as a consequence, on the conducting properties of the salts. At the same time, the mutual influence of the molecular structures of BDA-TTP and the counterion on the crystal structure and the conducting properties of these salts remains, in essence, an open question. In this connection, the synthesis of new BDA-TTP salts with anions of different types and investigation of their structures and properties are of considerable interest.

In the present study, we synthesized the first BDA-TTP salts with copper(II) metal complex anions, β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ (**1**) and $(BDA\text{-}TTP)_2CuCl_4$ (**2**). The crystals and electronic band structures and the conducting properties of these salts were studied and compared with those of the BEDT-TTF and bis(ethylenedithio)tetraselenafulvalene (BETS) salts with the same anions, *viz.*, $(BEDT\text{-}TTF)_2CuCl_4$,[9] $(BEDT\text{-}TTF)_3CuCl_4 \cdot H_2O$,[9,10—12] and θ-$(BETS)_4Cu_2Cl_6$,[13] the latter two salts being stable molecular metals.

Experimental

The BDA-TTP donor was synthesized according to a known procedure.[14]

Crystals of radical cation salts **1** and **2** were prepared by electrochemical oxidation of BDA-TTP in a benzonitrile—ethylene glycol mixture (9 : 1, v/v) under galvanostatic conditions (I = 0.5—1 mA, t = 20 °C for **1** and I = 0.5—0.75 mA, t = 25 °C for **2**). The onium salts $Ph_4AsCuCl_3$ and $(Bu_4N)_2CuCl_4$ were used as the electrolytes for **1** and **2**, respectively. Crystals of radical cation salt **1** were grown within 2—3 weeks as plates at a platinum anode; crystals of salt **2**, within 5—6 weeks as linear crystals in a mixture with crystals having another shape (**3**). We failed to solve the structure of **3** because of a poor quality of the crystals. The simultaneous formation of salts **2** and **3** is apparently because the $(CuCl_4)^{2-}$ anion partially dissociates in solution into the $(CuCl_3)^-$ and Cl^- anions.[13]

The single-crystal X-ray diffraction study was carried out at room temperature on Bruker Nonius X8APEX (Mo-Kα radiation, OSMIC monochromator, combined φ/ω-scanning technique) and Enraf Nonius CAD-4F (Mo-Kα radiation, ω-scanning technique, graphite monochromator) diffractometers for **1** and **2**, respectively. The X-ray data set for the crystal of **1** was corrected for absorption using the SADABS program.[15] The structures were solved by direct methods and refined by the full-matrix least-squares method with the use of the SHELX-97 program package.[16] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically calculated positions and were not refined. Main crystal data and the structure refinement statistics are given in Table 1.

Table 1. Crystal data and the structure refinement statistics for the structures of β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ (**1**) and $(BDA\text{-}TTP)_2CuCl_4$ (**2**)

Parameter	**1**	**2**
Molecular formula	$C_{48}H_{48}Cl_6Cu_2S_{32}$	$C_{24}H_{24}Cl_4CuS_{16}$
M	1990.6	1030.7
a/Å	8.9908(3)	20.841(3)
b/Å	12.0551(4)	11.405(1)
c/Å	17.1887(6)	15.516(2)
α/deg	101.476(1)	90
β/deg	96.089(1)	101.73(1)
γ/deg	91.397(1)	90
V/Å^3	1813.5(1)	3611.0(8)
Space group	$P\bar{1}$	$C2/c$
Z	1	4
d_{calc}/g cm^{-3}	1.823	1.896
μ/cm^{-1}	17.66	18.49
F(000)	1008	2084
θ Scan range/deg	1.73—32.62	2.05—25.97
Ranges of indices h, k, l	$-13 \le h \le 12$, $-18 \le k \le 18$, $-25 \le l \le 25$	$-25 \le h \le 25$, $-14 \le k \le 14$, $-19 \le l \le 0$
Total number of reflections	40311	7145
Number of independent reflections	11711	3528
R_{int}	0.0386	0.0532
Number of parameters in refinement	424	240
GOOF on F^2	1.022	1.023
R ($I > 2\sigma(I)$)	0.0477	0.0388

The tight-binding band structure calculations were based on the effective one-electron Hamiltonian of the extended Hückel method.[17] The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg—Helmholtz formula.[18] All valence electrons were explicitly taken into account in the calculations, and the basis set consisted of double-ζ Slater-type orbitals for C and S, and single-ζ Slater-type orbitals for H. The exponents, contraction coefficients, and atomic parameters for C, S, and H were taken from the previous publication.[19]

The conductivity of single crystals was measured by the standard four-probe method at a direct current on an automated apparatus with a gradual decrease in the temperature from 300 K. Platinum wire contacts of diameter 10 μm were glued to a crystal with a DOTITE XC-12 graphite paste.

Results and Discussion

A projection of the crystal structure of radical cation salt **1** along the b axis is shown in Fig. 1. The structure is characterized by the presence of the radical cation layers of BDA-TTP, which are parallel to the ab plane and alternate with the $[Cu_2Cl_6]^{2-}$ dianions. The crystal structure contains two crystallographically independent BDA-TTP molecules (**A** and **B**) in general positions. The geometry of the molecule **A** and the atomic numbering scheme are presented in Fig. 2. The atoms of one

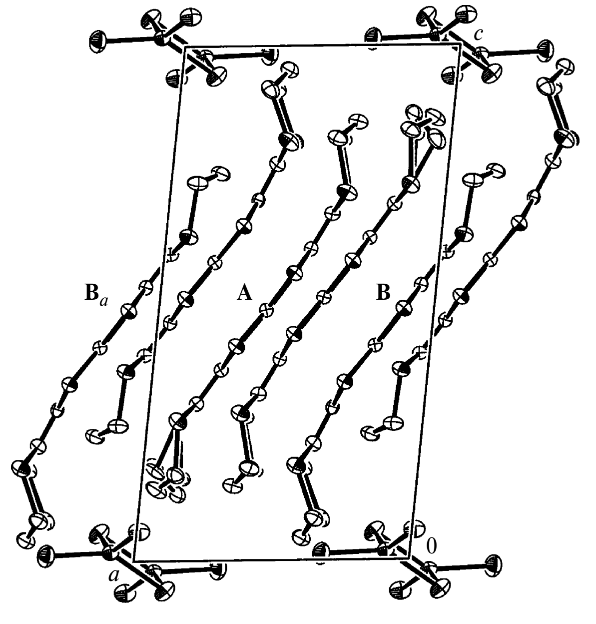

Fig. 1. Structure of the radical cation salt β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ projected along the *b* axis. The symmetry operations: **A**, **B** (*x*, *y*, *z*); $\mathbf{B}_a$ (*x* + 1, *y*, *z*).

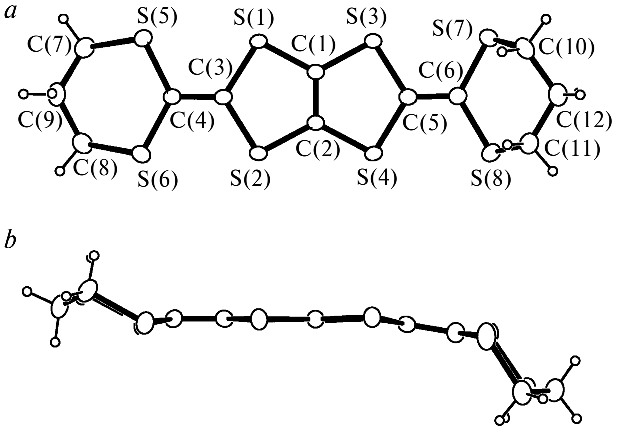

Fig. 2. Top view (*a*) and side view (*b*) of the BDA-TTP molecule and the atomic numbering scheme.

of the propylene groups of the molecule **A** are disordered over two positions in a ratio of 0.75/0.25. The torsion angles for two positions are 136.0° (139.1°) and 165.4° (161.4°) (C(6)—S(8)—S(7)—C(10)(C(11)) and C(6)—S(8)—S(7)—C(10a)(C(11a)), respectively). The dihedral angles characterizing folding of the six-membered rings about the S—S axis are 52 and 38° for **B** and 49° for the ordered propylene group of the donor **A**. The bond lengths in the molecules **A** and **B** are similar to the corresponding parameters in the BDA-TTP radical cations found in the radical cation salts β-$(BDA\text{-}TTP)_2SbF_6$ and β-$(BDA\text{-}TTP)_2AsF_6$.[7,20]

The conducting radical cation layer is characterized by the β-type packing of π donors (Fig. 3, *a*) analogous to the family of the superconductors β-$(BDA\text{-}TTP)_2X$ ($X = SbF_6$, AsF_6, PF_6, $GaCl_4$, or $FeCl_4$).[7,20—22] The layer is formed by the parallel stacks of BDA-TTP along the *a* axis. Each stack consists of the alternating donors **A** and **B**. The interplanar distances calculated from the atoms of the central TTP fragment are 3.47(1) and 3.48(1) Å for interactions II and I, respectively (see Fig. 3, *a*). The overlap modes of the molecules are shown in Fig. 3, *b*. There are numerous shortened intermolecular S...S contacts within the radical cation layer. The lengths and energies of these contacts are given in Table 2. In addition, there are the C(10)—H...Cl(2) and C(10A)—H...Cl(2) cation—anion contacts between the propylene group of the molecule **A** and the Cl atoms of the $[Cu_2Cl_6]^{2-}$ anion in the structure of **1** (H...Cl, 2.64 and 2.62 Å; C...Cl, 3.611 and 3.582 Å; C—H—Cl, 176.4° and 171.8°, respectively). Apparently, it is these interactions that are responsible for the observed disorder of the propylene group of the cation **A**.

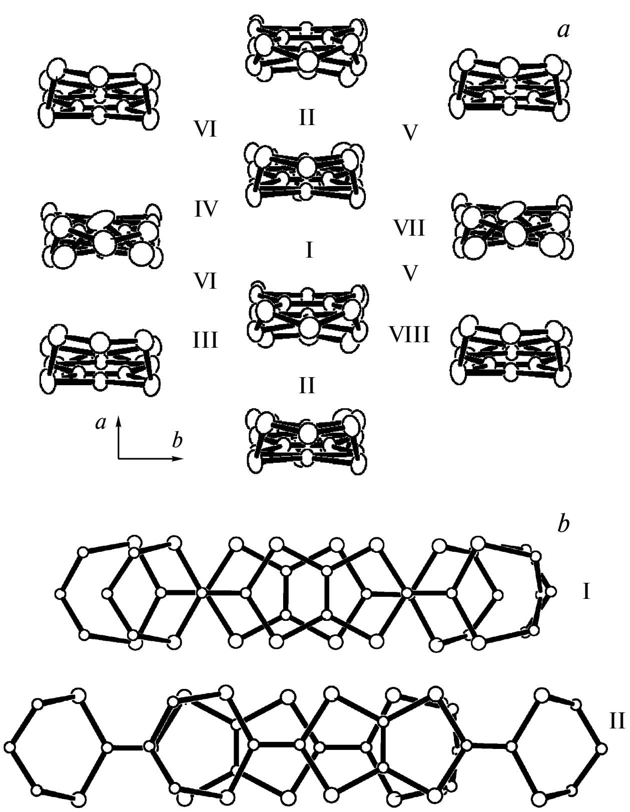

Fig. 3. *a*. Radical cation layer in the structure of β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ projected along the long molecular axis (I—VIII, interaction types). *b*. The overlap modes (I, II) of the BDA-TTP donors in the stack.

The anionic moiety of radical cation salt **1** consists of the centrosymmetric $[Cu_2Cl_6]^{2-}$ anions composed of two edge-shared flattened tetrahedra. The $Cu—Cl_{term}$ and $Cu—Cl_{bridg}$ interatomic distances are 2.197(1), 2.197(1) and 2.307(1), 2.310(1) Å, respectively. The distance be-

Table 2. Shortened S...S contacts between the BDA-TTP radical cations (<4.0 Å) and the orbital overlap integrals ($|\beta_{\text{HOMO–HOMO}}|$) in the crystal of **1**

Interaction type*	S...S /Å	$|\beta_{\text{HOMO–HOMO}}|$ /eV
I	3.724, 3.725, 3.728, 3.737, 3.866, 3.888, 3.974	0.3262
II	3.659, 3.669, 3.700, 3.711, 3.738, 3.763, 3.863, 3.878, 3.928, 3.990	0.5139
III	3.600 (×2), 3.624 (×2), 3.647	0.0303
IV	3.590, 3.622 (×2), 3.649 (×2), 3.722 (×2)	0.0142
V	3.867, 3.891, 3.895, 3.994	0.1093
VI	3.693, 3.729, 3.731, 3.818	0.1019
VII	3.539 (×2), 3.547 (×2), 3.697, 3.789 (×2)	0.0532
VIII	3.390 (×2), 3.490, 3.629 (×2)	0.0704

* For notations, see Fig. 3, *a*.

tween the copper atoms in the dimer is 3.348(1) Å. Earlier, the dimeric $[Cu_2Cl_6]^{2-}$ anion has been found in the structures of the radical cation salts θ-$(BETS)_4Cu_2Cl_6$ [13,23] and κ-$(BETS)_8[Cu_2Cl_6][CuCl_4]$.[24]

The projection of the crystal structure of radical cation salt **2** along the *b* axis is shown in Fig. 4. The crystals have a layered structure. The radical cation layers alternate with the $[CuCl_4]^{2-}$ anions along the *a* axis. The monoclinic unit cell contains one independent BDA-TTP radical cation in a general position. Both propylene groups of the donor (C(7), C(9) and C(11), C(12) atoms) are partially disordered over two positions in a ratio of 0.8/0.2 (C(4)—S(6)—S(5)—C(8), 168.7°; C(4)—S(6)—S(5)—C(7)/C(7a), 176.0°/151.7°), and 0.6/0.4 (C(6)—S(8)—S(7)—C(10), 134.8°; C(6)—S(8)—S(7)—C(11)/C(11a), 163.4°/135.9°).

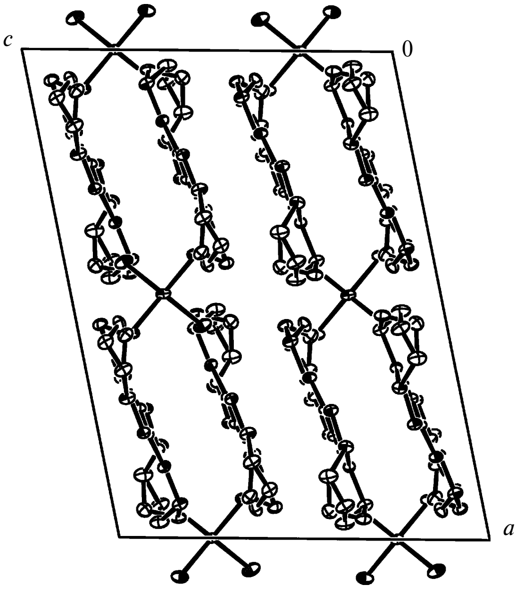

Fig. 4. Structure of the radical cation salt $(BDA\text{-}TTP)_2CuCl_4$ projected along the *b* axis.

The conducting layer is characterized by an unusual packing of the donor molecules. It consists of the BDA-TTP dimers, the adjacent dimers being twisted about the normal to the mean plane of the molecules by 115° and are inclined with respect to each other in the stack by 12.5° (Fig. 5, *a*). The overlap modes of the molecules in the dimers and between the dimers are shown in Fig. 5, *b*. The distance between the molecules in the dimers is 3.28(2) Å, which is substantially shorter than the analogous distances in salts based on BEDT-TTF. There are numerous shortened contacts between the BDA-TTP donors in the dimer (12 S...S, 12 S...C, and 7 C...C), and only a few contacts exist between the dimers (1 S...S and 4 S...C).

In the crystals of **2**, the $[CuCl_4]^{2-}$ anion can be described as a flattened tetrahedron (Cl—Cu—Cl angles

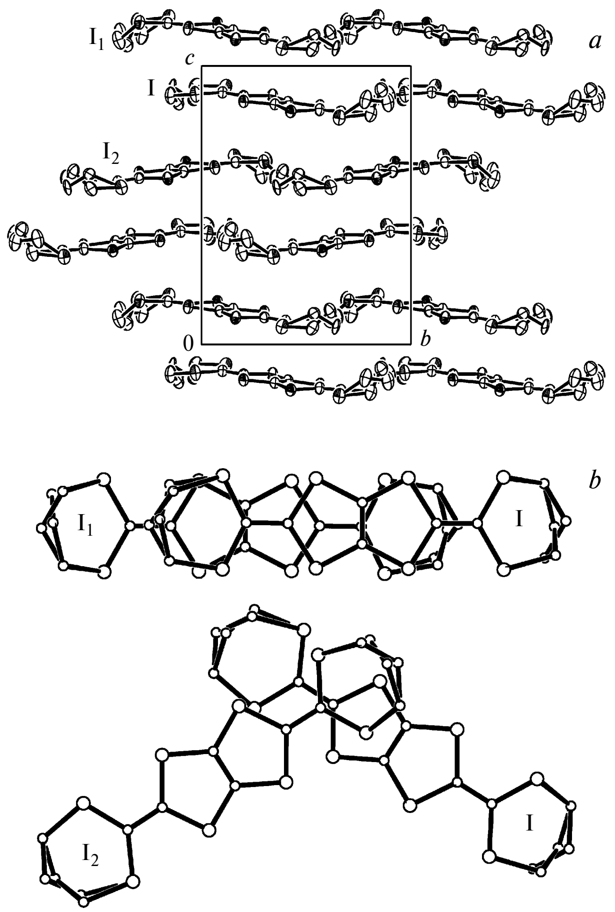

Fig. 5. Salt $(BDA\text{-}TTP)_2CuCl_4$ (**2**): the projection of the radical cation layer (*a*) and the overlap modes of the donors in the dimer (I_1—I) and between the dimers (I—I_2) in the radical cation layer (*b*). The symmetry operations: I_1 ($-x + 1/2$, $-y + 1/2$, $-z + 2$); I_2 ($-x + 1/2$, $y - 1/2$, $-z + 3/2$).

vary from 97 to 139°). The average Cu—Cl distance is 2.251(3) Å. This geometry is typical of copper(II) compounds[25] and has been observed earlier[9,11] in the structures of the radical cation salts $(BEDT\text{-}TTF)_3CuCl_4 \cdot H_2O$ and $(BEDT\text{-}TTF)_2CuCl_4$. The crystals of $(BDA\text{-}TTP)_2CuCl_4$ are not isostructural to the crystals of $(BEDT\text{-}TTF)_2CuCl_4$,[9,11] in which radical cation layers are absent and the BEDT-TTF stacks are separated by the $[CuCl_4]^{2-}$ anions. The crystals of this salt are semiconductors.

The conductivity of the crystals of salts **1** and **2** at room temperature is 3.5—6.5 and $\sim 10^{-3}$ Ohm^{-1} cm^{-1}, respectively. As in the case of some other BDA-TTP salts,[20] we failed to measure the temperature dependence of the conductivity for crystals of **1** because of strong cracking in the crystals in the range of 180—250 K. Because of the fragile nature of the crystals, sample destruction on cooling in the course of measurements occurs apparently due to strains at contacts. The temperature dependence of the conductivity was measured for salt **1** in a pellet (σ_{298} = 0.1 Ohm^{-1} cm^{-1}) in the range of 300—100 K. In this temperature range, the resistivity increases exponentially. The plot of the resistivity *vs.* the temperature for salt **1** measured for a crystal (before its destruction) is identical to that for a pellet (Fig. 6).

The band structure and the calculated Fermi surface for salt **1** are shown in Fig. 7, *a* and *b*, respectively. The Fermi surface of typical β-salts BDA-TTP can be described as a cylinder with an elliptical cross-section.[20] Unlike these salts, the unit cell of **1** has the doubled *b* parameter. Consequently, the Brillouin zone decreases by a factor of two in this direction, and the Fermi surface can be considered as a result of hybridization of a series of elongated ellipsoids (see Fig. 7, *b*). A strongly elongated shape of ellipsoids is associated with anisotropy of interactions within the conducting layer. The overlap integrals characterizing interactions within the stack are different for types I and II (0.3262 and 0.5139 eV, respectively; see Fig. 3, *a* and Table 2) and are similar to those found in 2D β-salts.[26] It should be noted that the interstack interactions in this salt (see Table 2) are substantially weaker than those within the stack. As a consequence, the Fermi surface is intermediate between the surfaces characteristic of two-dimensional (2D) and one-dimensional (1D) β-type conductors and consists of four open orbits (two electron and two hole orbits).

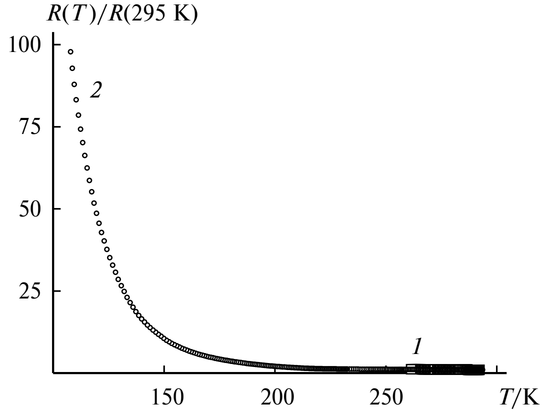

Fig. 6. Temperature dependence of the resistivity (*R*) for a crystal (*1*) and a pellet (*2*) of the radical cation salt $\beta\text{-}(BDA\text{-}TTP)_4Cu_2Cl_6$.

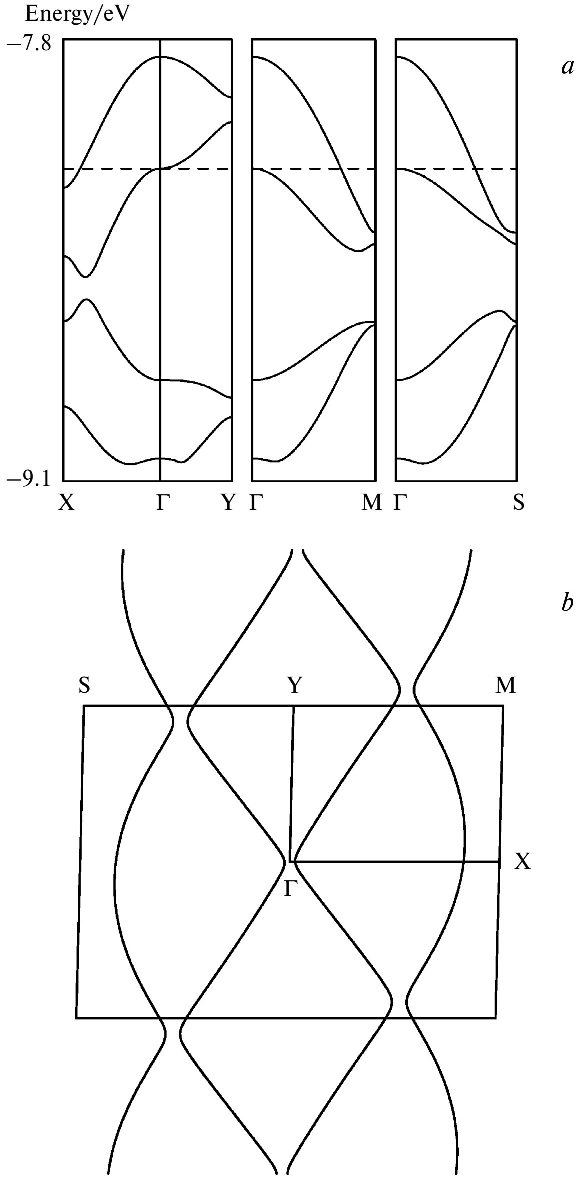

Fig. 7. *a*. Electronic structure of the radical cation salt $\beta\text{-}(BDA\text{-}TTP)_4Cu_2Cl_6$; the Fermi level is indicated by a dashed line, Γ = (0, 0), X = ($a^*/2$, 0), Y = (0, $b^*/2$), M = ($a^*/2$, $b^*/2$), S = ($-a^*/2$, $b^*/2$). *b*. The calculated Fermi surface of the crystals of $\beta\text{-}(BDA\text{-}TTP)_4Cu_2Cl_6$.

As expected, the electronic structure of salt **2** with complete charge transfer corresponds to a typical strongly

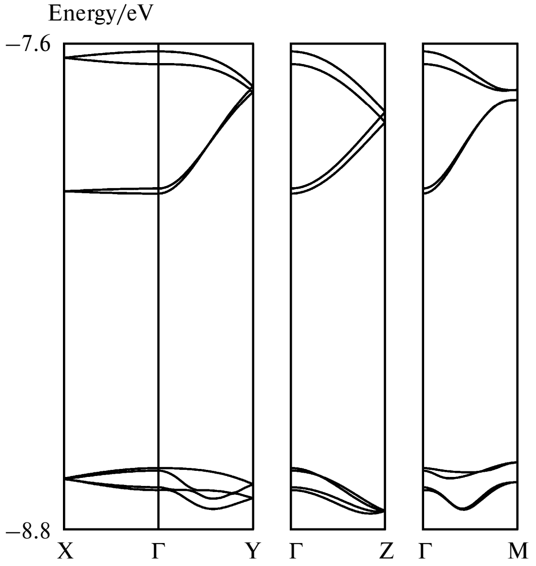

Fig. 8. Electronic structure of the radical cation salt $(BDA\text{-}TTP)_2CuCl_4$.

dimerized system with two well-isolated bands (Fig. 8), each consisting of four levels (unit cell of salt **2** includes eight BDA-TTP molecules, which form four dimers; see above). The overlap integral $\beta_{HOMO-HOMO}$ for each dimer is 0.8162 eV, whereas the energies of other interactions are an order of magnitude lower.

It is of interest to compare the semiconducting crystals of β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ (**1**) with the crystals containing octahedral and tetrahedral singly-charged anions of the β-$(BDA\text{-}TTP)_2XF_6$ (**4**) (X = P, Sb, or As) and β-$(BDA\text{-}TTP)_2XCl_4$ (**5**) (X = Fe or Ga) families. Crystals of **4** are ambient-pressure superconductors,[7,8] whereas the metal—dielectric transition is observed at 120 K for crystals of **5**.[21,22,27] The transition temperature decreases with increasing pressure. At a pressure higher than ~4.5 kbar, the superconducting transition occurs in magnetic ($FeCl_4^-$) and nonmagnetic ($GaCl_4^-$) compounds. In addition, crystals of **5** with the $FeCl_4^-$ anion are characterized by antiferromagnetic ordering with T_N = 8.5 K at ambient pressure.

The question is what is the origin of the difference in the transport properties of crystals of **1**, **4**, and **5**. All crystals have β-type conducting radical cation layers composed of stacks of the parallel donor molecules. However, the radical cation stacks in the crystals of **1** are equidistant and are closely packed, and the interplanar distances are 3.47—3.48 Å, whereas the stacks in the crystals of **4** and **5** are dimerized with distances of ~3.50—3.80 Å (**4**) and ~3.60—3.90 Å (**5**). All crystals have shortened intermolecular S...S contacts in the radical cation layers. However, unlike the crystals of **4** and **5** and the β-type superconductor based on BEDT-TTF ($(BEDT\text{-}TTF)_2I_3$),[28] in which all these contacts are slightly shortened, the crystals of **1** have a number of strongly shortened S...S contacts (3.390 and 3.490 Å; see Table 2), which can lead to localization of the electronic states within the layers. It is known that the presence of different types of disorder is an important factor influencing the conducting properties of organic conductors. As mentioned above, one of the terminal propylene groups of the molecule **A** in the crystals of **1**, unlike those in the crystals of **4** and **5**, is disordered. The crystals of **1** and **5** radically differ from those of **4** also in that they contain two crystallographically independent BDA-TTP molecules in the radical cation layer. All the above-considered structural features of the crystals of **1**, **4**, and **5** are responsible for the difference in their electronic structures and transport properties. Superconducting crystals of **4** have the approximately isotropic closed Fermi surface characteristic of β structures. The calculated energies of intermolecular interactions in the stacks and between the stacks for these crystals are comparable with those for the crystals of **5**. However, the theoretical Fermi surface for the crystals of **5** is more similar to that of crystals with κ-type rather than β-type conducting layers.[27] The electronic structure of the crystals of **1** (see Table 2 and Fig. 7) is intermediate between 2D and 1D structures of β-type conductors.

In summary, radical cation salts with Cu^{2+} metal complex anions were synthesized for the first time based on the donor of a new type, *viz.*, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene: β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ (**1**) and $(BDA\text{-}TTP)_2CuCl_4$ (**2**). The crystal and electronic band structures and the conducting properties of these radical cation salts were studied. Both salts are semiconductors. In the crystal structure of **1**, the activation conductivity can be associated with a more pronounced one-dimensional character of the electronic structure of this salt compared to known metal 2D β-BDA-TTP salts; in the crystal structure of **2**, with the complete charge transfer. Salt **2** contains the paramagnetic metal complex anion $[CuCl_4]^{2-}$ and belongs to bifunctional compounds containing a conducting radical cation system and a magnetic anionic subsystem. This type of compounds has attracted increasing interest for the purpose of searching for synergetic effects.[29]

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