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New molecular magnetic metals: κ-$(BDH\text{-}TTP)_4CuCl_4 \cdot (H_2O)_n$ and κ-$(BDH\text{-}TTP)_2[CuCl_4]_{0.67} \cdot (H_2O)_{0.33}$ (BDH-TTP is 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene)

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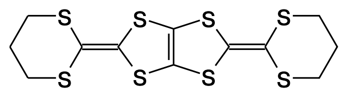
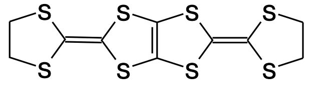
New radical cation salts based on 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP), *viz.*, κ-$(BDH\text{-}TTP)_4CuCl_4 \cdot (H_2O)_n$ (**1**) and κ-$(BDH\text{-}TTP)_2[CuCl_4]_{0.67} \cdot (H_2O)_{0.33}$ (**2**), were synthesized and structurally characterized. Single crystals were prepared by the electrochemical oxidation of BDH-TTP under galvanostatic conditions. The X-ray diffraction study showed that the salts have layered structures characterized by the presence of κ-type BDH-TTP conducting layers. These layers alternate with the complex anions composed of $[CuCl_4]^{2-}$ units and water molecules. Both salts exhibit the temperature dependence of the metallic conductivity down to 4.2 K. Spin-spin antiferromagnetic correlations in the Cu^{2+} subsystem were observed in the crystals of **2**.

Key words: 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene, radical cation salt, synthesis, electrochemical oxidation, crystal structure, conductivity, paramagnetism.

In recent years, new approaches have been developed for the design of electron donors for the synthesis of molecular conductors and superconductors based on the decrease in the size of the π-electron system of the donor and the expansion of its σ-bonded moiety.[1,2] 2,5-Bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene (BDA-TTP) and 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP) were synthesized with the use of these approaches, and these compounds have recently been employed for the synthesis of quasi-two-dimensional radical cation salts with a broad spectrum of conducting properties.[1—5] Unlike the BDA-TTP molecule containing the quite flexible six-membered (dithiane) rings, the BDH-TTP molecule is more planar due to the presence of the more rigid five-membered (dithiolane) rings.



BDA-TTP



BDH-TTP

Recently,[5] we have reported on the synthesis of first radical cation salts BDA-TTP, *viz.*, β-$(BDA\text{-}TTP)_4Cu_2Cl_6$ and $(BDA\text{-}TTP)_2CuCl_4$, with doubly charged copper(II) complex anions. In the present study, we describe the synthesis, crystal structures, and conducting and magnetic properties of two new BDH-TTP-based radical cation salts with the $[CuCl_4]^{2-}$ anion: κ-$(BDH\text{-}TTP)_4CuCl_4 \cdot (H_2O)_n$ (**1**) and κ-$(BDH\text{-}TTP)_2[CuCl_4]_{0.67} \cdot (H_2O)_{0.33}$ (**2**).

Experimental

Rhomb-like crystals of radical cation salts **1** and **2** were prepared by the electrochemical oxidation of BDH-TTP ($C = 10^{-3}$ mol L^{-1}) under galvanostatic conditions. The electrocrystallization was performed under the following conditions: benzonitrile + 5 vol.% of ethylene glycol as the solvent, $V = 20$ mL, $Ph_4AsCuCl_3$ ($C_2 = 2.5 \cdot 10^{-3}$ mol L^{-1}) as the electrolyte, $I = 0.5$—0.75 μA, $t = 20$ °C (compound **1**); 1,1,2-trichloroethane + 10 vol.% of ethyl lactate, $V = 20$ mL, $(Bu_4N)_2CuCl_4$ ($C_3 = 2.27 \cdot 10^{-3}$ mol L^{-1}) as the electrolyte, $I = 0.5$—0.6 μA, $t = 25$ °C (compound **2**). Crystals of radical cation salt **1** were grown within 3 weeks at a platinum anode, and crystals of salt **2** were grown within 5—6 weeks.

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The X-ray microprobe analysis was performed with a JEOL JSM-5800L scanning electron microscope at the x1000 magnification and the electron beam energy of 10 keV. The penetration depth of the beam was 1—3 μm.

The X-ray diffraction study was carried out at room temperature. The unit cell parameters and the intensities of reflections for single crystals of **1** and **2** were measured on Oxford Diffraction Gemini-R (Mo-Kα radiation, combined ϕ/ω-scanning technique, graphite monochromator) and Bruker KappaCCD (Mo-Kα radiation, combined ϕ/ω-scanning technique, graphite monochromator) diffractometers, respectively. The average structures were solved by direct methods with the use of the SHELXS-97 program and refined by the least-squares method with the use of the SHELXL-97 program.[6] The site occupancy of the anion in the structure of **1** was estimated as 1/2 due to the disorder of the anion with respect to the center of inversion. The site occupancies of the anion and the water molecule in the structure of **2** were refined as the related variables (*x*) and (1—*x*) according to the standard procedure implemented in the SHELXL program (0.67 and 0.33, respectively). The hydrogen atoms were positioned geometrically. The hydrogen atoms of the water molecules in the anion layer in the structure of **2** were not located. The absorption corrections were applied using the SCALE3 ABSPACK algorithm implemented in the CrysAlisPro program[7] and the SADABS software[8] (Bruker KappaCCD diffractometer) for the crystals of **1** and **2**, respectively. The crystal of **1** proved to be a pseudomerohedral twin with the twin matrix (100/0–10/10–1) and the twin-component ratio of 9 : 1. The X-ray diffraction pattern of the crystal of **2** shows diffuse superstructure reflections, which were not included in the structure solution and refinement.

Main crystallographic data and the structure refinement statistics are given in Table 1.

Table 1. Crystallographic data and the structure refinement statistics for compounds **1** and **2**

Compound	**1**	**2**
Molecular formula	$C_{40}H_{32}S_{32}CuCl_4$	$C_{20}H_{16}S_{16}Cu_{0.67}Cl_{2.68}O_{0.33}$
Symmetry	Triclinic	Orthorhombic
a/Å	8.283(1)	8.178(1)
b/Å	10.799(1)	11.092(2)
c/Å	18.445(3)	36.612(6)
α/deg	89.90(1)	90
β/deg	78.01(1)	90
γ/deg	89.60(1)	90
V/Å^3	1613.8(4)	3321.1(9)
Space group	$P\bar{1}$	*Pbnb*
Z	1	4
Number of measured reflections	9138	38972
Number of independent reflections	4581	4010
R_{int}	0.070	0.065
Number of parameters refinement	364	192
GOOF on F^2	1.020	1.033
$R(I > 2\sigma(I))$	0.079	0.067

The conductivity of the crystals was measured by the standard four-probe method at a direct current on an automated apparatus in the temperature range of 300—4.2 K. Platinum wire contacts of a diameter 10 μm were glued to a crystal with a DOTITE XC-12 graphite paste.

The static magnetic susceptibility of a polycrystalline sample of **2** was studied on a SQUID magnetometer (Quantum Desing MPMS 5XL) in the temperature range of 300—2 K in the magnetic field of 1 kOe. The diamagnetic moment of the free cell and the diamagnetic contribution were subtracted from the magnetic susceptibility using the Pascal coefficients.

Results and Discussion

The electrochemical oxidation of BDH-TTP was carried out in the presence of the electrolytes $Ph_4AsCuCl_3$ and $(Bu_4N)_2CuCl_4$ in a benzonitrile solution with the addition of 5 vol.% of ethylene glycol. Crystals of κ-(BDH-TTP)$_4$CuCl$_4 \cdot (H_2O)_n$ (**1**) suitable for the single-crystal X-ray diffraction study were obtained (with the use of $Ph_4AsCuCl_3$ as the electrolyte). The use of 1,1,2-trichloroethane instead of benzonitrile in the presence of (*S*)-ethyl lactate (10 vol.%) as the additive, which increases the solubility of BDH-TTP in 1,1,2-trichloroethane, resulted in the formation of crystals of κ-(BDH-TTP)$_2$-[CuCl$_4$]$_{0.67} \cdot (H_2O)_{0.33}$ (**2**) (in the presence of the electrolyte $(Bu_4N)_2CuCl_4$). Although the synthesis of crystals of **1** and **2** was carried out with the use of the electrolytes containing different chlorocuprate anions ($[CuCl_3]^-$ and $[CuCl_4]^{2-}$, respectively), both resulting salts contained the same $[CuCl_4]^{2-}$ anion. Unlike BDA-TTP, which forms the salt with the dinuclear anion ($[Cu_2Cl_6]^{2-}$)[5], BDH-TTP does not give salts with the $[CuCl_3]^-$ anion or its dimer. The formation of the $[CuCl_4]^{2-}$ anion in the synthesis of salt **1** is attributed to the dissociation of the starting $[CuCl_3]^-$ anion resulting in the appearance of Cl^- ions in the reaction solution followed by the reaction of these ions with $[CuCl_3]^-$.

The preliminary X-ray microprobe analysis of the crystals of both salts showed that they contain oxygen along with sulfur, copper, and chlorine. Hence, both salts involve molecules containing oxygen atoms. These could be water, ethylene glycol, or (*S*)-ethyl lactate molecules. The X-ray diffraction study showed that both crystal structures contain cavities, whose size is sufficient for the inclusion of water molecules in salts **1** and **2**. Due to the strong positional disorder in the anion layer of the crystals of **1**, water molecules were not located. The composition of these crystals (see Table 1) was identified as κ-(BDH-TTP)$_4$CuCl$_4 \cdot (X)_n$ (**1**), whereas the refinement of the site occupancies of the anion and the oxygen atom of water in the crystal structure of **2** led to the composition κ-(BDH-TTP)$_2$[CuCl$_4$]$_{0.67} \cdot (H_2O)_{0.33}$. This is qualitatively confirmed by the results of the X-ray microprobe analysis.

The crystals of **1** and **2** have layered structures (Fig. 1, *a* and *b*) and contain κ-type conducting layers, in which the radical cation layers consist of the BDH-TTP dimers arranged with respect to each other at angles of 83.02(5) and 81.71(3)° in **1** and **2**, respectively (Fig. 2, *a*). According to the stoichiometry, the radical cation layers in the crystals of **1** and **2** are formed by the BDH-TTP molecules with charges of +0.5 and +0.67, respectively. This is reflected in the character of the distribution of the bond lengths. Due to the disorder in the anion layer, the accuracy of the determination of the bond lengths is insufficient for the detailed analysis of their values. Nevertheless, it can be seen that the C=C double bonds in the more charged molecule (compound **2**) are longer (aver., 1.351 Å) than those in the crystal of **1** (1.333 Å). In the orthorhombic crystal structure of **2**, the layers consist of the crystallographically equivalent dimers, whereas the corresponding layer in the triclinic structure of **1** is formed by two independent dimers. However, the structures of **1** and **2** are characterized by the same overlap mode of BDH-TTP in the dimers (Fig. 2, *b*). The interplanar distances in the dimers calculated for the atoms of the central TTP fragment are 3.50(5) Å for the two dimers in the structure of **1** and 3.53(5) Å in the structure of **2**. The terminal ethylene groups in the radical cations are ordered in the structures of both **1** and **2**.

In the radical cation layers, there are numerous short intermolecular S...S contacts.

The radical cation layers alternate along the *c* axis with the anion layers containing $[CuCl_4]^{2-}$ anions and water molecules, which are not shown in Fig. 1.

The anion layer in the crystals of **1** is formed by the $[CuCl_4]^{2-}$ anions in general positions (Fig. 3, *a*). The anion is located near the center of inversion with the occupancy of 0.5, which is indicative of its positional disorder. There is an empty cavity of a volume 53 Å^3 near another center of inversion (0, 1/2, 0) in the anion layer. This cavity is characterized by the excess electron density, which may be indicative of the presence of a disordered solvent molecule. A comparison of the sizes of the water and ethylene glycol molecules with the size of the cavity shows that a water molecule can be present as a guest in the structure of **1**.

In the anion layer of the crystals of **2**, the $[CuCl_4]^{2-}$ anions occupy channels running along the *b* axis (Fig. 3, *b*). The anion is in a special position on a twofold axis and has

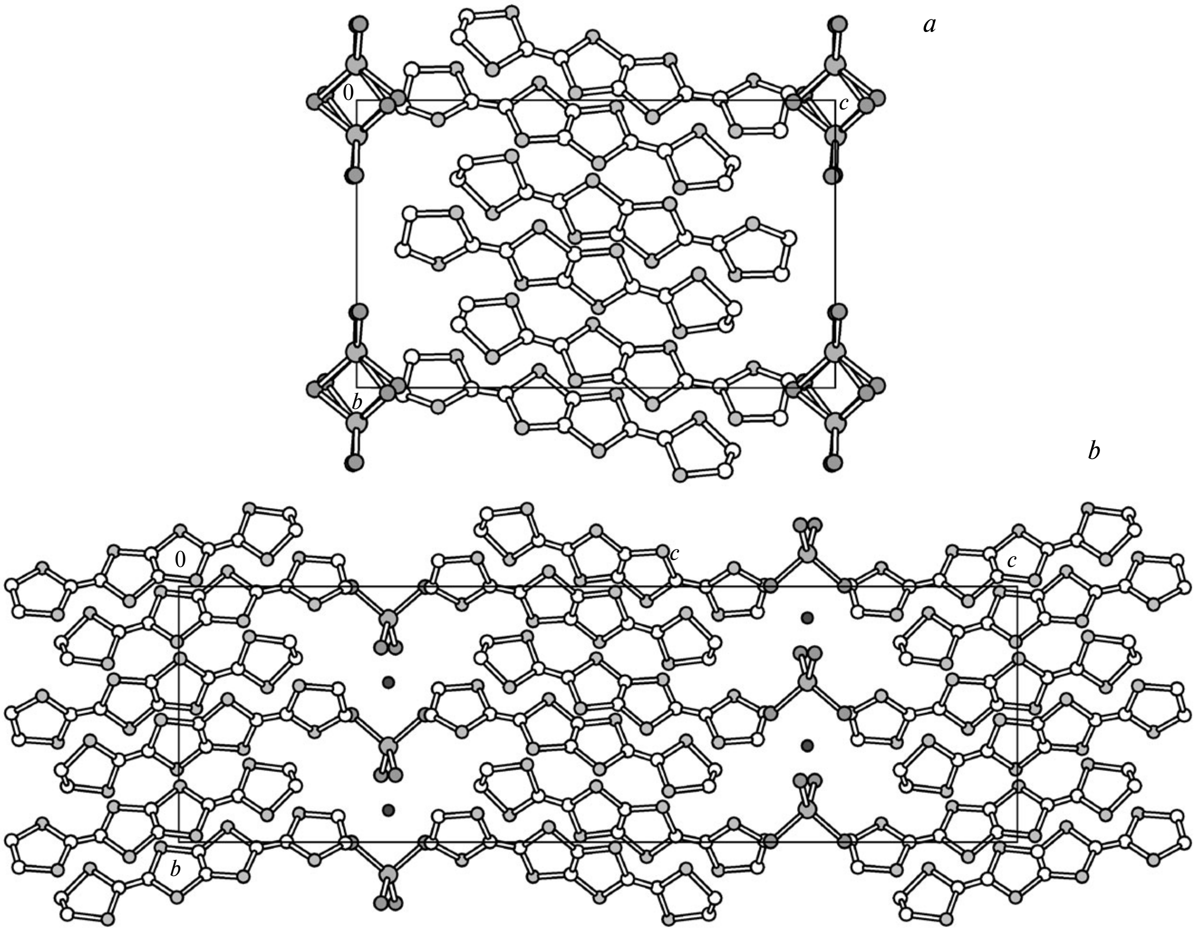


Fig. 1. Crystal structures of **1** (*a*) and **2** (*b*) projected along the *a* axis.

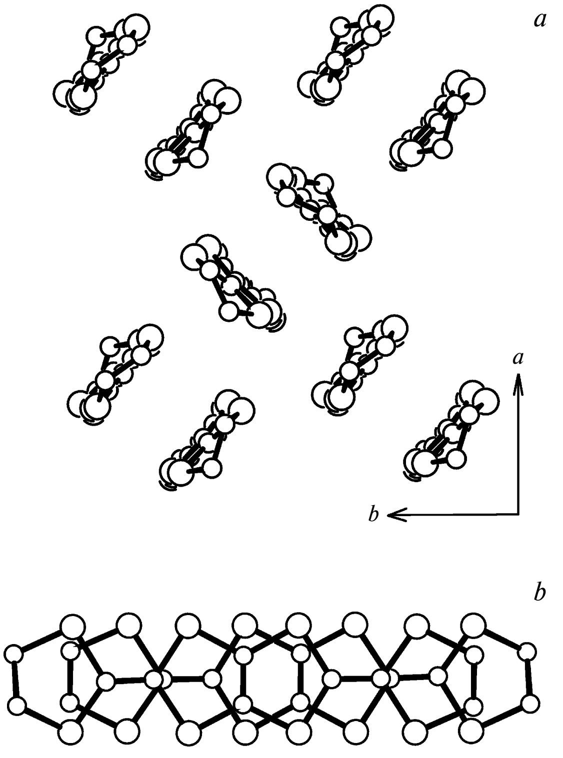


Fig. 2. Projection of the radical cation layer (*a*) and the overlap mode in the dimers (*b*) in the crystals of **1**.

the occupancy of 2/3, which is evidence of the possible presence of guest water molecules in the anion layer inside the channel, as in the crystal of **1**. The strong residual electron density peak near the anion was described by the O atom. After the refinement, the occupancy of this position was 1/3.

The coordination polyhedron of the copper atom can be described as a flattened tetrahedron with the interatomic Cu—Cl distances in the range of 2.03—2.27 Å in salt **1** and with the average Cu—Cl distance of 2.2 Å in salt **2**. The Cl—Cu—Cl angles vary from 93 to 140°. This geometry is characteristic of Cu^{II} compounds.[9] Previously, this geometry has been observed in the structures of the radical cation salts $(BEDT-TTF)_3CuCl_4 \cdot H_2O$ (BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene), $(BEDT-TTF)_2CuCl_4$,[10—13] and $(BDA-TTP)_2CuCl_4$.[5] The possible shortest Cu...Cu distances in the anion layer in the crystals of **2** are $b/2 = 5.546(3)$ Å and $a = 8.178(1)$ Å.

At room temperature, salts **1** and **2** have virtually the same conductivity (40 and 50 Ohm^{-1} cm^{-1}, respectively). The resistivity of the crystals decreases as the temperature decreases, which is indicative of the metallic behavior down to 4.2 K (Fig. 4).

The temperature dependence of the effective magnetic moment (μ_{eff}) for a polycrystalline sample of salt **2** is presented in Fig. 5. The magnetic moment μ_{eff} at room temperature (1.56 μ_B) is close to the calculated value (1.73 μ_B) for the noninteracting paramagnetic particles with the spin 1/2, which corresponds to the spin state of the Cu^{2+} ion. The monotonic decrease in the effective magnetic moment with a decrease in the temperature is indicative of antiferromagnetic correlations in the Cu^{2+} subsystems.

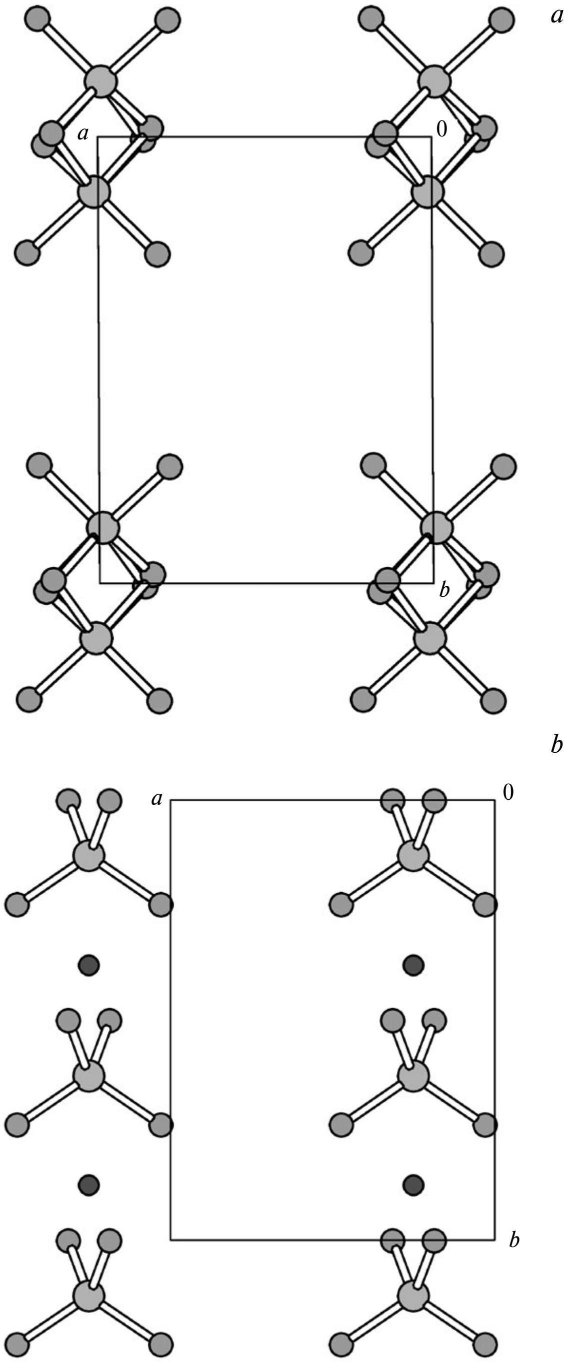


Fig. 3. Anion layers in the crystals of **1** (*a*) and **2** (*b*) projected along the *c* axis.

In addition to radical cations salts **1** and **2** under study, the following seven BDH-TTP-based salts have been struc-

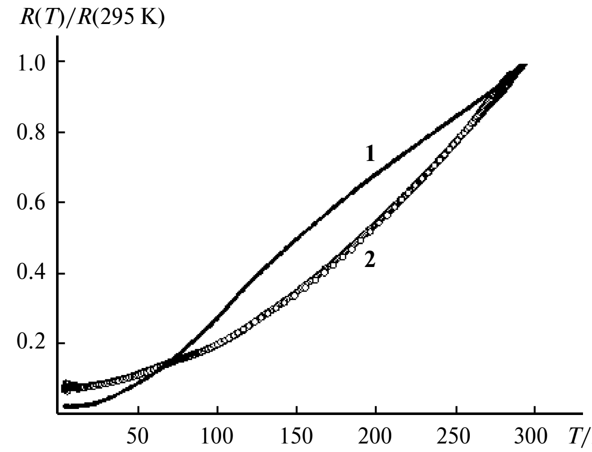


Fig. 4. Temperature dependence of the resistivity (R) of radical cation salts **1** and **2**.

turally characterized previously: κ-(BDH-TTP)$_2$FeCl$_4$ (**3**),[14] κ-(BDH-TTP)$_2$PF$_6$,[15] κ-(BDH-TTP)$_4$[FeNO(CN)$_5$],[16] κ-(BDH-TTP)$_4$[FeNO(CN)$_5$]$\cdot$NB,[16] κ-(BDH-TTP)$_4$Hg$_3$Br$_8$,[17] κ-(BDH-TTP)$_4$Hg$_3$Cl$_8$,[17] and κ-(BDH-TTP)$_4$[Hg(SCN)$_4$]$\cdot$NB.[18] All the above-mentioned salts have the same κ-type radical cation conducting layers regardless of the nature of the counterion and are magnetic metals stable down to low temperatures. From the crystallographic point of view, it is of particular interest to compare radical cation salts **2** and **3** (the unit cell parameters: a = 11.039 Å, b = 37.471 Å, c = 8.169 Å; space group *Pnma*), which have the similar unit cell parameters and similar structures. However, some positions occupied by the larger doubly charged [CuCl$_4$]$^{2-}$ anions, as compared to the singly charged [FeCl$_4$]$^-$ anions, are replaced by neutral H$_2$O molecules. This leads to a change in the crystal symmetry of **2** (space group *Pnaa* for **3**), and the structural block (BDH-TTP)$_2$ has different charges (+0.67 and +1 for **2** and **3**, respectively).

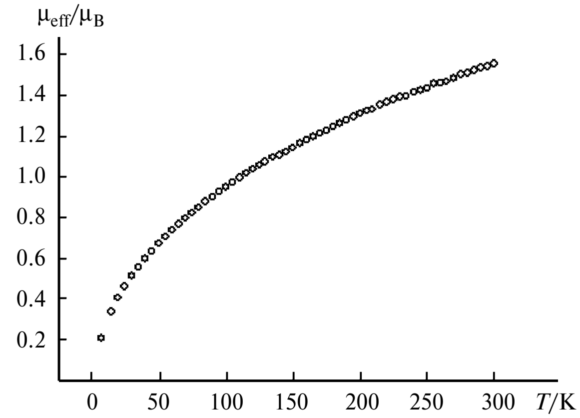
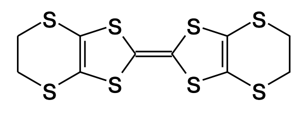
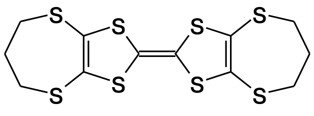


Fig. 5. Temperature dependence of the effective magnetic moment (μ_{eff}) for the crystals of **2**.

The crystals of the radical cation salts BDH-TTP with the [CuCl$_4$]$^{2-}$ anion are not isostructural with the crystals of the salt BDA-TTP containing the same anion[5] in spite of the fact that BDH-TTP and BDA-TTP are structural isomers of BEDT-TTF and bis(propylenedithio)tetrathiafulvalene (BPDT-TTF), respectively.[1,2]



BEDT-TTF



BPDT-TTF

It is known[16] that the radical cation salts of the latter, *viz.*, β-(BEDT-TTF)$_2$I$_3$ and β-(BPDT-TTF)$_2$I$_3$, as well as ε-(BEDT-TTF)$_2$I$_7$ and ε-(BPDT-TTF)$_2$I$_7$, are isostructural with each other.

Therefore, the cation radical salts with the Cu^{2+} metal complex anions based on the donor 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene were synthesized: κ-(BDH-TTP)$_4$CuCl$_4\cdot$(H$_2$O)$_n$ (**1**) and κ-(BDH-TTP)$_2$-[CuCl$_4$]$_{0.67}\cdot$(H$_2$O)$_{0.33}$ (**2**). The crystal structures and the conducting and magnetic properties of these compounds were studied. Both salts contain the paramagnetic metal complex anion [CuCl$_4$]$^{2-}$ and belong to bifunctional compounds containing the conducting radical cation system and the magnetic anion subsystem. Salts **1** and **2** have the κ-type packing of the conducting layers alternating in the crystals with the anion layers, which is characteristic of BDH-TTP-based organic conductors. As opposed to the cation layers, the structures of the anion layers in these salts are substantially different. In the range of 300—4.2 K, both salts exhibit the temperature dependence of the conductivity typical of metals. In the crystals of **2**, spin-spin antiferromagnetic correlations in the anion sublattice associated with Cu^{2+} (S = 1/2) are observed.

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