Synthesis, crystal structure, and conducting properties of a new molecular conductor $(DBTTF)_{11}(TeCl_6)_4$

P. P. Kushch,* S. V. Konovalikhin, G. V. Shilov, L. O. Atovmyan, T. A. Khannanova, and R. N. Lyubovskaya

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: kushch@icp.ac.ru

The structure and conducting properties of a new radical cation salt of dibenzotetrathiafulvalene (DBTTF), *viz.*, $(DBTTF)_{11}(TeCl_6)_4$ (**1**), were studied. According to the X-ray diffraction data, the crystal of **1** contains six crystallographically independent DBTTF radical cations alternating with stacks of the $(TeCl_6)^{2-}$ anions. At room temperature, the conductivity of the crystals is 15 S cm^{-1} and it changes exponentially as the temperature decreases. It was found that an increase in the size of the anion in compounds of type **1** results in the appearance of interactions between the stacks and in an enhancement of the two-dimensional character of the conductivity.

Key words: synthesis, structure, dibenzotetrathiofulvalene, chlorotellurate, radical cation salt, conductivity.

The problem of the design of organic compounds with unusual physical properties[1] requires studies aimed at the preparation of radical cation salts and their comprehensive investigation. Low-dimensional conducting compounds attract interest because of their specific physical properties, such as the quantum Hall effect, the transfer of the spin density wave initiated by the magnetic field, quantum oscillations, *etc.*[2] Dibenzotetrathiafulvalene (DBTTF) can serve as a donor, forming quasi-one-dimensional radical cation salts.[3] The one-dimensional character of DBTTF salts with bulky octahedral anions, for example, $(DBTTF)_8(SnCl_6)_3$ (**2**), made it possible to experimentally reveal the effect of fluctuations of the unit cell parameters on the Peierls transition and to determine the true temperature of this transition.[4] When the Cl atom is replaced by the Br atom in the double-charged $(SnCl_6)^{2-}$ anion of salt **2**, equidistant stacks typical of the structure of **2** are divided into triads in the bromine-containing salt and, as a consequence, the composition and structure are changed.[5] The replacement of the double-charged $(SnCl_6)^{2-}$ anion by the single-charged $(NbCl_6)^-$ anion leads only to a change in the composition: $(DBTTF)_7(NbCl_6)_3$ (**3**).[5] The unit cell of salt **3** contains seven donor molecules, which are located at equal but substantially larger distances than those in salt **2**.[5]

In the present work, we synthesized a new radical cation salt $(DBTTF)_{11}(TeCl_6)_4$ (**1**) based on the DBTTF donor and the $(TeCl_6)^{2-}$ anion and studied the effect of the size of the octahedral anion on the conducting properties of the crystals, their composition, and the crystal structure.

Experimental

Single crystals of the $(DBTTF)_{11}(TeCl_6)_4$ salt were obtained as elongated black parallelepipeds from a mother liquor by electrochemical oxidation of a solution of DBTTF[3] in acetonitrile ($1.3 \cdot 10^{-3}$ mol L^{-1}) on a platinum anode under conditions of constant current (I = 0.4 μA cm^{-2}) at 22 °C for three weeks. The $(Bu_4N)_2TeCl_6$ salt ($3.8 \cdot 10^{-3}$ mol L^{-1}) was used as a supporting electrolyte.

X-ray diffraction data were collected from a parallelepiped-shaped crystal of dimensions 0.5×0.08×0.06 mm. The crystallographic data are as follows: M = 4582.5, a = 15.035(5) Å, c = 38.052(10) Å, V = 8602(4) Å^3, tetragonal system, space group $P4_2/m$, Z = 2, d_{calc} = 1.77 g cm^{-3}. The unit cell parameters were determined on a four-circle automated KM-4 diffractometer (Kuma Diffraction, (Cu-Kα) radiation, λ = 1.5418 Å, graphite monochromator). A total of 1316 independent reflections with $I \geq 2s(I)$ were collected using the θ/2ω scanning technique in the angle range $2.2 \leq 2\theta \leq 161.6°$. The structure was solved by the direct method followed by a series of successive Fourier syntheses with the use of the SHELX-86[6] and SHELXL-93 program packages.[7] The positions of the hydrogen atoms were not located. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. The final value of the R factor was 0.052. Absorption was ignored, μ(Cu-Kα) = 128.3 cm^{-1}. The atomic coordinates, the bond

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 370—372, February, 2000.

1066-5285/00/4902-0372 $25.00

lengths, and the bond angles in the crystal structure of (DBTTF)$_{11}$(TeCl$_6$)$_4$ were deposited with the Cambridge Structural Database (CSD).

The conductivity of the (DBTTF)$_{11}$(TeCl$_6$)$_4$ salt was measured along and crosswise the crystal by the standard four-contact method with a direct current of 1 μA.

Results and Discussion

In the single crystals of the (DBTTF)$_{11}$(TeCl$_6$)$_4$ salt, the DBTTF radical cations and the (TeCl$_6$)$^{2-}$ anions are packed in infinite stacks along the *c* axis of the unit cell (Fig. 1). In the structure of **1**, there are three crystallographically independent (TeCl$_6$)$^{2-}$ anions, which occupy special positions, *viz.*, all anions are located on a fourfold symmetry axis, one of them being additionally located on a mirror plane *m*. Six crystallographically independent DBTTF cations (denoted A, B, C, D, E, and F) also occupy special positions, namely, a twofold symmetry axis. In addition, the cation A is located on a mirror plane *m*. Therefore, there are 1/4 of two anions each, 1/2 of one anion, 1/4 of one DBTTF cation, and 1/2 of five DBTTF cations each per asymmetric unit. The overall composition of the asymmetric unit is (DBTTF)$_{2.75}$(TeCl$_6$). On going to integer coefficients, the composition of the salt can be written as (DBTTF)$_{11}$(TeCl$_6$)$_4$. Since the charge of the anion is −2, the charge of each DBTTF cation is approximately +0.73.

In one of the octahedral (TeCl$_6$)$^{2-}$ anions, the Te(1)—Cl$_{ax}$ bonds (2.635(8) Å) are longer than the Te(1)—Cl$_{eq}$ bonds (2.480(6) and 2.496(5) Å). In the second anion, one axial bond length (2.522(9) Å) and the equatorial bond lengths (2.526(3) and 2.535(3) Å) are equal within the experimental error, whereas the second axial Te(2)—Cl bond (2.655(7) Å) is longer than the other bonds. In the third anion, the axial Te(3)—Cl bonds (2.500(10) Å) are shorter than the equatorial bonds (2.564(4) Å). The equality of the axial and equatorial Te—Cl bond lengths in the (TeCl$_6$)$^{2-}$ anions as well as the observed elongation of the equatorial bonds compared to the axial bonds are well known for the (TeCl$_6$)$^{2-}$ anions.[8–11] In each anion, the equatorial atoms are in a single plane and form Cl...S contacts (3.17—3.47(1) Å) with the DBTTF cations, which are shorter than the sum of the van der Waals radii of the S and Cl atoms (1.85 and 1.90 Å, respectively).[12] Apparently, the difference in the Te—Cl bond lengths in the anions is associated with cation—anion interactions. Note that the Cl atoms do not form short contacts in the anions.

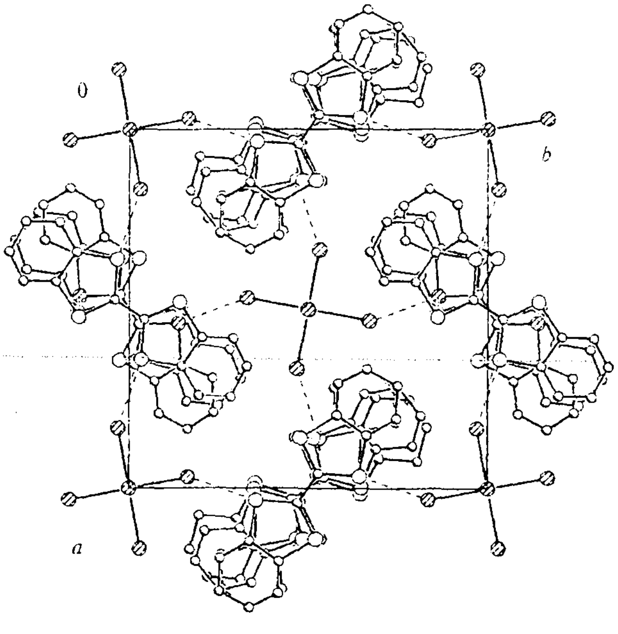

Fig. 1. Crystal structure of the (DBTTF)$_{11}$(TeCl$_6$)$_4$ salt.

In the stacks, the DBTTF cations alternate as follows: F″...E″...D″...C″...B″...A...B...C...D...E...F...F′...E′. The distances between the mean planes of the cations are 3.47(1) Å (A...B), 3.48(1) Å (B...C), 3.51(1) Å (C...D), 3.23(1) Å (D...E), 3.48(1) Å (E...F), and 3.51(1) Å (F...F′). In the stack, the mean planes of the cations are coplanar and the cations in the stack are rotated with respect to each other. The angles between the long axes of the cations (parallel to the central C=C bond) are as follows: A/B, 23.4(5)°; B/C, 6.4(5)°; C/D, 20.6(5)°; D/E, 25.2(4)°; E/F, 16.8(5)°; and F/F′, 0.0(6)°. No correlation between the angles of rotation of the molecules and the distances between their mean planes was found. The short S...S contacts between the radical cations, which vary from 3.37(1) to 3.65(1) Å, are present only in the stacks. Each cation forms four S...S contacts, which are shorter than the sum of the van der Waals radii of the S atoms.[12]

A poor accuracy of determination of the bond lengths and bond angles in the cations does not allow us to perform detailed analysis. It can only be noted that all cations are nonplanar and the C atoms of the benzene rings deviate from the mean plane of the molecule in opposite directions. Only the S atoms and the C atoms of the central C=C bond are in a single plane. The exception is the cation A, whose atoms are all located on a symmetry plane.

The structure of salt **1** is similar to those of the radical cation salts (DBTTF)$_8$(SnCl$_6$)$_3$ (see Refs. 5 and 13) and (DBTTF)$_3$(SnBr$_6$) (**4**)[5] studied previously. However, unlike **1**, the distances between the mean planes of the cations in the cationic stacks in the structure of **2** are equal (3.49 Å), whereas the cations in the structure of **4** are linked in triads. The cations within the triads are rotated with respect to each other. The cations from the adjacent triads in the stack are located exactly above each other. The distances between the mean planes of the cations within the triads are 3.47 and 3.44 Å and the distances between the triads are 3.58 Å.[14] In compound **1**, the D...E dimer may be distinguished. In this dimer, the distance between the mean planes of the molecules

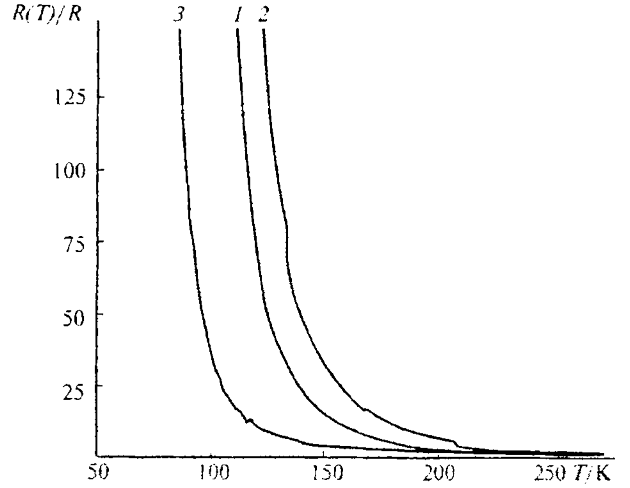

Fig. 2. Temperature dependence of the resistance of the crystals of $(DBTTF)_{11}(TeCl_6)_4$ measured along the crystal at p = 1 bar (*1*) and 0.3 kbar (*2*) and crosswise the crystal at p = 1 bar (*3*).

is 3.23 Å, which is 0.25 Å shorter than the other distances. The other interplanar distances in the cationic stack are equal within the experimental error.

The conductivity measured along the axis of the crystal at room temperature ($\sigma_{\|}$) is 15 S cm^{-1}. The resistance of the crystal increases exponentially as the temperature decreases (Fig. 2, curve *1*); the activation energy ΔE = 0.084 eV. In addition, the resistance along the axis of the crystal was measured under a pressure (p) of 0.3 kbar. This pressure appeared on the crystal upon cooling when a spherical drop of apiezon heated to 50 °C was applied to the crystal. From Fig. 2 (curve *2*) it can be seen that when the pressure is applied, the resistance curve is shifted to the right by ~15 K with virtually the same ΔE = 0.080 eV. Curve *3* (see Fig. 2) corresponds to the resistance measured crosswise the crystal. The conductivity ($\sigma_{\perp}$) at room temperature is 5 S cm^{-1}. The temperature dependence of the conductivity follows the exponential law with ΔE = 0.066 eV. This insignificant difference in the conductivity at room temperature suggests that salt **1** does not belong to pronounced quasi-one-dimensional systems and the anisotropy of the conductivity in **1** is small, unlike the classical quasi-one-dimensional systems.[15] This is also evidenced by the fact that the conductivity of this system measured previously using polycrystalline samples (pellets)[16] changed exponentially with ΔE = 0.07 eV. Probably, the fact that the activation energy measured crosswise the axis of the crystal ($\Delta E_{\perp}$) is smaller than the $\Delta E_{\|}$ energy measured along the axis of the crystal indicates that the axis of the greatest growth of the crystal does not correspond to the direction of its highest conductivity.

Therefore, a comparison of the conductivity of salt **1** with the conductivities of the salts synthesized previously (for salts **2**, **3**, and **4**, σ = 350—500,[3] 40—150,[5] and 40 S cm^{-1},[3] respectively) allows the conclusion to be made that an increase in the size of the central metal atom in octahedral anions leads to a change in the composition of the salt, dimerization of the DBTTF radical cations in the conducting stack, and, as a consequence, to a decrease in the conductivity along this stack. In addition, interactions between the conducting stacks are observed and the compound is somewhat "two-dimensional."

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32685a).

References

1. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. H. Whangbo, *Organic Superconductors*, Prentice Hall, Englewood Cliffs, New Jersey, 1992, 400.
2. T. Ishiguro and K. Yamaji, *Organic Superconductors*, Springer-Verlag, Berlin, 1990, 217.
3. R. N. Lyubovskaya, *Usp. Khim.*, 1983, **52**, 1301 [*Russ. Chem. Rev.*, 1983, **52** (Engl. Transl.)].
4. R. N. Lyubovskaya, R. B. Lyubovskii, V. A. Merzhanov, and M. L. Khidekel', *Zh. Exp. Teor. Fiz.*, 1979, **76**, 1414 [*JETP*, 1979, **76** (Engl. Transl.)].
5. R. P. Shibaeva, L. P. Rozenberg, and R. M. Lobkovskaya, *Kristallografiya*, 1980, **25**, 507 [*Sov. Phys. Crystallogr.*, 1980, **25** (Engl. Transl.)].
6. G. M. Sheldrick, *SHELX-86, Program for Crystal Structure Determination*, University of Cambridge, England, 1986.
7. G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Determination*, University of Cambridge, England, 1993.
8. M. H. B. Ghozlen and J. W. Bats, *Acta Crystallogr., Sect. B*, 1982, **B38**, 1308.
9. W. Abriel and C. Friedrich, *Z. Naturforsch., B*, 1985, **40**, 1691.
10. H. K. Ault and S. Husebye, *Acta Chem. Scand., Ser. A*, 1978, **32**, 157.
11. O. Reich, S. Hasche, S. Bonmann, and B. Krebs, *Z. Anorg. Allg. Chem.*, 1998, **624**, 411.
12. L. Pauling, *The Nature of the Chemical Bond*, University Press, Cornell, 1960.
13. L. S. Veretennikova, R. N. Lyubovskaya, R. B. Lyubovskii, L. P. Rozenberg, M. A. Simonov, R. P. Shibaeva and M. L. Khidekel', *Dokl. Akad. Nauk SSSR*, 1978, **241**, 862 [*Dokl. Chem.*, 1978 (Engl. Transl.)].
14. R. P. Shibaeva, L. P. Rozenberg, M. Z. Aldoshina, R. N. Lyubovskaya, and M. L. Khidekel', *Zh. Strukt. Khim.*, 1979, **20**, 485 [*J. Struct. Chem.*, 1979, **20** (Engl. Transl.)].
15. I. F. Shchegolev, *Phys. St. Sol.*, 1972, **12**, 9.
14. R. N. Lyubovskaya, M. Z. Aldoshina, E. I. Zhilayeva, V. A. Merzhanov, and M. L. Khidekel', *Mater. Sci.*, 1981, **7**, 239.

Received June 26, 1999;
in revised form September 24, 1999