Synthesis and crystal structure of an organic semiconductor $(ET)_4[Hg_2I_6]$

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A new cation-radical salt $(ET)_4[Hg_2I_6]$ (**1**), where ET is bis(ethylenedithio)tetrathiafulvalene, has been synthesized in the system ET—HgI_3^-—PhCl. An X-ray study of **1** (a = 41.02(5), b = 23.01(1), c = 8.233(2) Å, V = 7772(3) Å^3, space group $Pc2_1b$, Z = 4, d_{calc} = 2.308 g cm^{-3}) has established its composition, chemical formula, and the main structural features. The ET cation-radicals are packed in the conducting layer, the type of packing is α"; the $[Hg_2I_6]^{2-}$ anion has a dimeric structure. The temperature dependence of the conductivity of the $(ET)_4[Hg_2I_6]$ crystals (σ_{300} = 6 Ohm^{-1} cm^{-1}) has a semiconducting character.

Key words: organic conductors; ion-radical salts; bis(ethylenedithio)tetrathiafulvalene; mercury iodides; crystal structure; electrochemical synthesis.

Earlier,[1] we reported the preparation of a series of new organic metals of the general formula $(ET)_8[Hg_4X_{12}(PhY)_2]$ during electrochemical synthesis of bis(ethylenedithio)tetrathiafulvalene (ET) salts in an ET—HgX_3^-—PhY system using $(Bu_4N)HgX_3$ (X = Cl, Br) salts as electrolytes and halogenated benzenes PhY (Y = Cl, Br) as solvents. Physical studies have shown that their electroconducting properties depend largely on the composition. In order to study the "composition—structure—electroconductivity" relationship in more detail we are carrying out a systematic study of all the crystalline products obtained in this system. At present, the crystal structures of four organic metals have been determined: $(ET)_8[Hg_4Cl_{12}(PhCl)_2]$, $(ET)_8[Hg_4Br_{12}(PhBr)_2]$, $(ET)_8[Hg_4Cl_{12}(PhBr)_2]$, and $(ET)_8[Hg_4Br_{12}(PhCl)_2]$. The data on the stuctures of the two former compounds have been already published,[2,3] and data on the remaining two salts will be reported later. A characteristic feature in the structure of the chloro- and bromomercurate ET salts, in comparison to other known ET salts, is the formation of complex four-charged anions consisting of four HgX_3 groups and two PhY solvent molecules. X-ray data on a new cation-radical salt synthesized in the ET—HgX_3^-—PhCl system using the iodomercurate $(Bu_4N)HgI_3$ as an electrolyte are reported in the present article. By analogy with previous investigations in the ET—HgX_3^-—PhY (X, Y = Cl, Br) system, it was assumed that the crystals obtained in the ET—HgX_3^-—PhCl system would have the composition $(ET)_8[Hg_4I_{12}(PhCl)_2]$. However, the X-ray investigation showed that the compound formed has the composition $(ET)_4[Hg_2I_6]$ (**1**).

The conductivity of single crystals of **1** at room temperature is σ_{300}= 6 Ohm^{-1} cm^{-1}. The dependence of the conductivity of **1** on temperature is of a semiconducting character.

Experimental

Compound **1** was obtained by electrochemical oxidation of a solution of ET in chlorobenzene under constant current, I = 1 μA, using a standard U-shaped cell with a platinum anode. ET (9.7 mg, $0.25 \cdot 10^{-4}$ *M*) and $[(C_4H_9)_4N]HgI_3$ (80.6 mg, $1.5 \cdot 10^{-3}$ *M*) were dissolved in 15 mL of chlorobenzene. The electrochemical oxidation was carried out at a current density of 2.2 μA cm^{-2} for 5 days at 40 °C. The reaction resulted in the formation of single crystals of compound **1** at the anode: $2ET + 2ET^+ + 2HgI_3^- \rightarrow (ET)_4[Hg_2I_6]$. The composition and chemical formula of **1** were established by X-ray structural analysis.

Crystal data: $(C_{10}H_8S_8)_4Hg_2I_6$, molecular weight 2701.35, orthorhombic, a = 41.02(5), b = 23.01(1), c = 8.233(2) Å, V = 7772(3) Å^3, space group $Pc2_1b$ (standard group $Pca2_1$, № 29), Z = 4, d_{calc} = 2.308 g cm^{-3}, F(000) = 5048. A crystal shaped as a thin right angled black plate with dimensions 0.30×0.10×0.03 mm, μ(Mo-Kα) = 7.16 mm^{-1} was chosen for collecting data. The intensities of 4928 independent reflections with $I > 2\sigma(I)$ used in calculations were measured on an automatic four-circle KM-4 (KUMA DIFFRACTION, Poland) diffractometer, ω/2θ scan technique with monochromatic Mo-Kα radiation, $2\theta_{max}$ = 44°.

The structure was determined by the direct method and refined by the least-squares method to R = 0.093 and R_w = 0.095 in anisotropic approximation, applying the absorption correction (DIFABS[4] program) using the weight scheme $w = 1.3218/(\sigma^2(F) + 0.007435\ F^2)$. The attempt at solving the

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Table 1. Coordinates of nonhydrogen atoms in structure **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	0.2401(2)	0.6551(4)	0.6871(9)	C(1)	0.361(3)	0.296(5)	0.085(9)
Hg(2)	0.2415(2)	0.4976(4)	0.859(1)	C(2)	0.351(3)	0.362(5)	0.025(9)
I(1)	0.3059(3)	0.6711(5)	0.693(2)	C(3)	0.421(4)	0.295(5)	0.03(1)
I(2)	0.1995(3)	0.7308(5)	0.572(2)	C(4)	0.421(3)	0.346(4)	0.07(1)
I(3)	0.2256(2)	0.5419(5)	0.531(1)	C(5)	0.484(3)	0.322(7)	0.06(1)
I(4)	0.2269(2)	0.6137(5)	1.019(1)	C(6)	0.512(3)	0.326(6)	0.114(9)
I(5)	0.3065(3)	0.4786(5)	0.846(2)	C(7)	0.579(4)	0.292(5)	0.01(1)
I(6)	0.1935(2)	0.4261(5)	0.979(1)	C(8)	0.577(3)	0.350(4)	0.09(1)
S(1)	0.3875(8)	0.251(2)	−0.033(5)	C(9)	0.640(3)	0.281(5)	0.08(1)
S(2)	0.4594(9)	0.260(1)	0.019(5)	C(10)	0.642(3)	0.349(4)	0.115(9)
S(3)	0.5395(8)	0.263(2)	0.001(5)	C(11)	0.314(4)	0.600(7)	0.30(1)
S(4)	0.6092(9)	0.249(2)	0.006(5)	C(12)	0.317(3)	0.550(5)	0.354(9)
S(5)	0.6095(9)	0.393(2)	0.134(5)	C(13)	0.383(4)	0.604(5)	0.30(1)
S(6)	0.5390(8)	0.380(1)	0.141(5)	C(14)	0.385(3)	0.545(4)	0.31(1)
S(7)	0.459(1)	0.377(1)	0.138(6)	C(15)	0.448(3)	0.577(6)	0.31(1)
S(8)	0.388(1)	0.397(2)	0.114(6)	C(16)	0.476(3)	0.574(5)	0.34(1)
S(9)	0.3494(9)	0.644(2)	0.237(5)	C(17)	0.538(4)	0.595(6)	0.26(1)
S(10)	0.420(1)	0.634(2)	0.250(5)	C(18)	0.540(4)	0.539(5)	0.32(1)
S(11)	0.499(1)	0.630(2)	0.247(5)	C(19)	0.613(4)	0.596(6)	0.30(1)
S(12)	0.5712(9)	0.640(1)	0.235(6)	C(20)	0.611(3)	0.536(5)	0.32(1)
S(13)	0.5712(7)	0.498(2)	0.384(5)	C(21)	−0.106(3)	0.360(5)	0.439(9)
S(14)	0.5005(9)	0.515(1)	0.373(5)	C(22)	−0.112(4)	0.297(6)	0.396(9)
S(15)	0.421(1)	0.511(1)	0.348(5)	C(23)	−0.037(4)	0.359(6)	0.48(1)
S(16)	0.3493(8)	0.498(2)	0.368(5)	C(24)	−0.037(3)	0.301(4)	0.402(9)
S(17)	−0.0702(9)	0.404(2)	0.484(5)	C(25)	0.026(3)	0.335(7)	0.45(1)
S(18)	−0.0002(9)	0.391(1)	0.472(5)	C(26)	0.050(4)	0.331(7)	0.40(1)
S(19)	0.0799(8)	0.397(1)	0.452(5)	C(27)	0.118(3)	0.357(5)	0.472(9)
S(20)	0.151(1)	0.403(2)	0.483(7)	C(28)	0.121(4)	0.301(6)	0.40(1)
S(21)	0.1515(8)	0.255(1)	0.405(5)	C(29)	0.187(3)	0.358(4)	0.527(9)
S(22)	0.079(1)	0.272(1)	0.411(6)	C(30)	0.186(3)	0.310(5)	0.394(9)
S(23)	0.0006(8)	0.269(1)	0.397(4)	C(31)	−0.146(4)	0.548(6)	0.79(1)
S(24)	−0.074(1)	0.258(2)	0.370(5)	C(32)	−0.145(3)	0.616(5)	0.772(9)
S(25)	−0.1131(9)	0.508(2)	0.717(5)	C(33)	−0.078(4)	0.553(5)	0.78(1)
S(26)	−0.040(1)	0.518(2)	0.722(5)	C(34)	−0.078(3)	0.609(4)	0.822(9)
S(27)	0.0377(9)	0.520(2)	0.730(5)	C(35)	−0.017(3)	0.578(6)	0.81(1)
S(28)	0.1086(9)	0.507(2)	0.706(5)	C(36)	0.011(3)	0.576(6)	0.77(1)
S(29)	0.108(1)	0.649(2)	0.861(5)	C(37)	0.075(3)	0.559(5)	0.70(1)
S(30)	0.038(1)	0.637(2)	0.867(5)	C(38)	0.075(3)	0.614(5)	0.77(1)
S(31)	−0.043(1)	0.637(2)	0.852(5)	C(39)	0.147(5)	0.546(6)	0.80(1)
S(32)	−0.1132(9)	0.651(2)	0.866(5)	C(40)	0.146(3)	0.616(5)	0.758(9)

structure within the framework of the centrosymmetric space group *Pcmb* (standard group *Pbcm*, № 57) resulted in a reasonable model. However, the high value of $R = 0.20$ after the model was refined by the least-squares method showed that it was worth while to make calculations in the noncentrosymmetric space group $Pc2_1b$. Further calculations confirmed the correctness of this choice. The atomic coordinates are given in Table 1. All the calculations were made on a PC AT-286 using the package of SHELX[5] programs.

Results and Discussion

The crystal structure of **1** (Fig. 1) is a packing characteristic of the majority of ET salts with alternating organic (conducting) and inorganic (nonconducting) layers. In salt **1**, these layers are formed, respectively, by four crystallographically independent ET cation-radicals denoted A, B, C, and D, and $[Hg_2I_6]^{2-}$ anions. The layers are parallel to the *bc* plane and alternate along the *a* axis.

The ET cation-radicals are stacked parallel to the *c* axis. Cation overlapping occurs in two different ways (Fig. 2): in the stacks built of plane-parallel A or D molecules the cations are shifted relative one another by 1/2 of a molecule across its long axis, while in the stacks built of B or C cations the shift is a quarter of the molecule along this axis. It should be noted that neither of these ovelappings favors optimal interaction of the π-orbitals of all of the S atoms, which is important for understanding the conducting properties of crystals **1**. The stacks of cations A and those of cations B alternate parallel to the *b* axis and form one type of conducting layer, while the stacks of C cations and those of D cations alternate along the *b* axis to form another type.

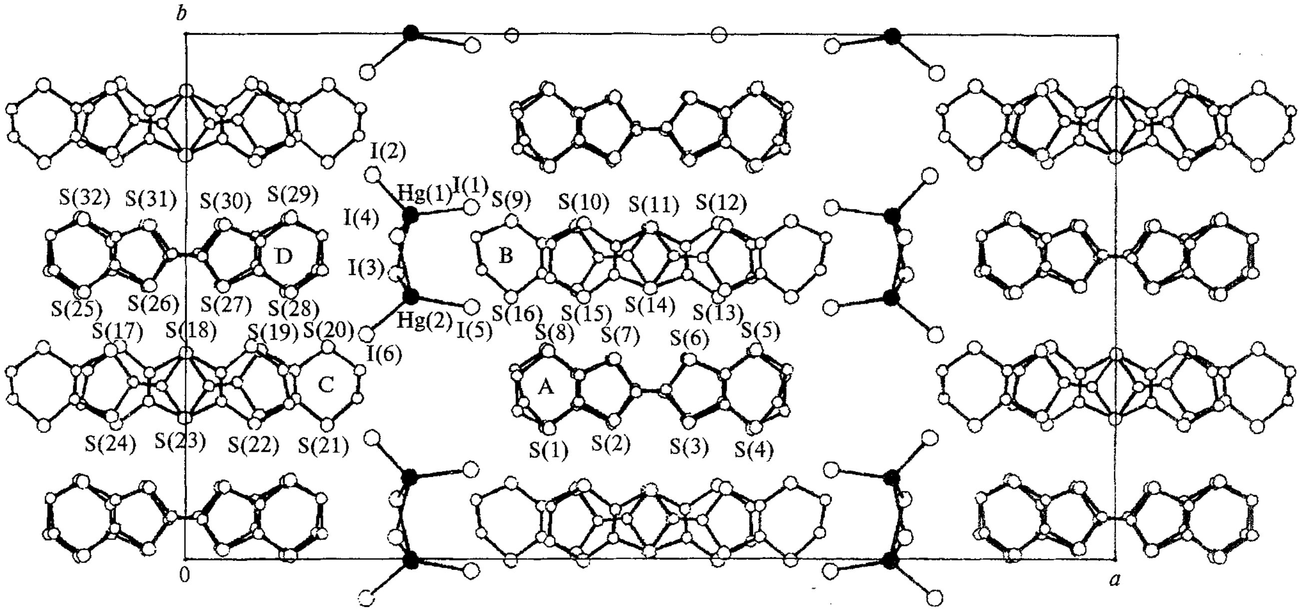

Fig. 1. Projection of the $(ET)_4[Hg_2I_6]$ structure on the *ab* plane.

The structural type of both of the conducting layers (Fig. 3) is the same and is, according to the literature notation, of the α" type.[6] The dihedral angles A/B, A/B', A/A', and B/B' between the mean planes of the ET cations of the neighboring stacks in the layers built of A and B (see Fig. 3) are 38.5, 2.1, 40.4, and 36.6°. The analogous angles C/D', C/D, D/D', and C/C' in the other type of layers are 34.0, 8.5, 42.3, and 25.6°. In each stack, the ET cations are practically parallel to each other (the dihedral angles between the molecular planes of the neighboring cations in the A, B, C, and D stacks are 1.8, 0.5, 0.5, and 3.1°, respectively) and bound to each other by ordinary van der Waals interactions. The average interplane distances in the A, B, C, and D stacks are 3.87, 3.74, 3.93, and 3.76 Å, respectively. The shortened intermolecular S...S contacts between the stacks are listed in Table 2.

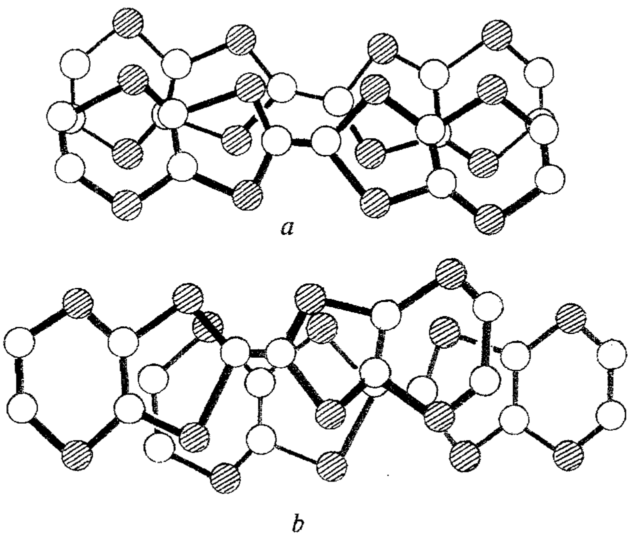

Fig. 2. Types of overlapping of ET cation-radicals: in A or D stacks (*a*), in B or C stacks (*b*).

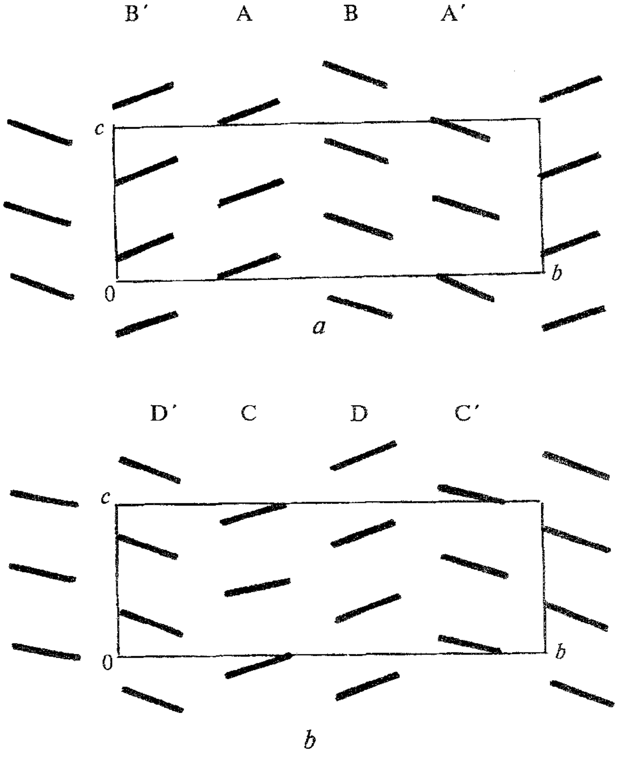

Fig. 3. α"-Pattern of ET cation packing in the conducting layers of the structure **1**: packing of the A and B cations (*a*); packing of the C and D cations (*b*).

Table 2. Shortened intermolecular contacts S...S < 3.68 Å, I...C < 3.90 Å

Contact	Distance/Å
S(1)...S(12)(1−*x*, *y*−0.5, −*z*)	3.49(5)
S(4)...S(9) (1−*x*, *y*−0.5, −*z*)	3.53(5)
S(4)...S(10) (1−*x*, *y*−0.5, −*z*)	3.56(5)
S(4)...S(12) (*x*, *y*−0.5, 0.5−*z*)	3.64(5)
S(5)...S(13)	3.52(5)
S(6)...S(13)	3.62(5)
S(8)...S(13) (1−*x*, *y*, *z*−0.5)	3.45(6)
S(8)...S(15)	3.55(5)
S(8)...S(16)	3.49(6)
S(17)...S(25)	3.48(6)
S(17)...S(26)	3.50(6)
S(19)...S(25) (−*x*, *y*, *z*−0.5)	3.46(5)
S(19)...S(28)	3.57(5)
S(20)...S(28)	3.54(6)
S(21)...S(29) (*x*, *y*−0.5, 1.5−*z*)	3.59(6)
S(21)...S(32) (−*x*, *y*−0.5, 1−*z*)	3.64(6)
S(22)...S(29) (*x*, *y*−0.5, 1.5−*z*)	3.64(6)
S(24)...S(29) (−*x*, *y*−0.5, 1−*z*)	3.45(6)
S(24)...S(32) (*x*, *y*−0.5, 1.5−*z*)	3.65(6)
I(1)...C(9) (1−*x*, 0.5+*y*, 1−*z*)	3.75(8)
I(1)...C(11)	3.55(9)
I(2)...C(40)	3.81(9)
I(3)...C(31) (−*x*, *y*, *z*−0.5)	3.81(9)
I(5)...C(2) (*x*, *y*, *z*+1)	3.68(7)
I(5)...C(20) (1−*x*, *y*, 0.5+*z*)	3.74(7)

The $[Hg_2I_6]^{2-}$ anion has a dimeric structure (see Fig. 1). Each Hg atom is surrounded by four I atoms, which form a distorted tetrahedral coordination. The Hg—I bond lengths and the I—Hg—I bond angles (Table 3) vary in the ranges 2.59(2)—2.97(1) Å and 94.7(4)—123.5(5)° for the Hg(1) atom and in the ranges 2.70(2)—3.04(1) Å and 92.8(4)—128.6(5)° for the Hg(2) atom. The fact that the bonds between the mercury atoms and the bridging I(3) and I(4) atoms are longer than the bonds with the terminal I(1), I(2) and I(5), I(6) atoms, and that the I—Hg—I bond angles between the terminal bonds are greater than the angles between the bridging bonds is typical of such dimers.[7–12] The Hg(1)I(3)Hg(2)I(4) four-membered cycle is nonplanar; the dihedral angle between the I(3)Hg(1)I(4) and I(3)Hg(2)I(4) planes is 34.1°. The planes I(1)Hg(1)I(2) and I(3)Hg(1)I(4), as well as the planes I(3)Hg(2)I(4) and I(5)Hg(2)I(6) are almost orthogonal: the respective dihedral angles are 95.5 and 84.1°. The Hg(1)...Hg(2) distance in the anion is 3.89(1) Å.

The structure of the anionic layer is insular and is formed by the isolated $[Hg_2I_6]^{2-}$ dimers. Interaction between the anionic and cationic layers in structure **1** occurs *via* the shortened contacts between the I atoms and the C atoms of the ethylene groups (see Table 2), in contrast to the $(ET)_4Hg_3I_8$ structure[12] where such contacts are absent.

Table 3. Bond lengths and bond angles in the $[Hg_2I_6]^{2-}$ anion

Bond	*d*/Å	Bond	*d*/Å
Hg(1)—I(1)	2.72(2)	Hg(1)—I(2)	2.59(2)
Hg(1)—I(3)	2.97(1)	Hg(1)—I(4)	2.95(1)
Hg(2)—I(3)	2.96(1)	Hg(2)—I(4)	3.04(1)
Hg(2)—I(5)	2.70(2)	Hg(2)—I(6)	2.75(1)
Angle	**ω/deg**	**Angle**	**ω/deg**
I(1)—Hg(1)—I(2)	123.5(5)	I(1)—Hg(1)—I(3)	109.1(4)
I(1)—Hg(1)—I(4)	102.1(4)	I(2)—Hg(1)—I(3)	107.5(5)
I(2)—Hg(1)—I(4)	116.0(5)	I(3)—Hg(1)—I(4)	94.7(4)
I(3)—Hg(2)—I(4)	92.8(4)	I(3)—Hg(2)—I(5)	103.7(4)
I(3)—Hg(2)—I(6)	111.9(4)	I(4)—Hg(2)—I(5)	110.9(5)
I(4)—Hg(2)—I(6)	103.3(4)	I(5)—Hg(2)—I(6)	128.6(5)
Hg(1)—I(3)—Hg(2)	82.1(4)	Hg(1)—I(4)—Hg(2)	81.1(3)

It should be mentioned that salt **1**, in its composition, $(ET)_4[Hg_2I_6]$, is formally similar to $(ET)_4[Hg_3I_8]$ salt (**2**) if the anion in the latter is represented as $[Hg_2I_6]^{2-} \cdot HgI_2$. Comparison of the structures of crystals **1** and **2** disclosed that these compounds are related not only by a stoichiometric, but also by a more profound structural similarity: structure **1** is the same as a part of structure **2**. This is especially spectacular if projections of structures **1** (see Fig. 1) and **2** (Fig. 4) along the cation-radical stacks are compared. Indeed the mutual arrangement of the ET cations and the $[Hg_2I_6]^{2-}$ anions on both projections is practically the same. It is assummed that the doubling of the period b = 23.01(1) Å in **1** as compared with a = 11.989(4) Å in **2** is connected with the fact that the ET cation-radicals in the conducting layer have α''-type packing (see Fig. 3), which is less ordered than the θ-pattern that occurs in structure **2**.

Summing up the X-ray structural data on **1** it is necessary to stress that the use of the iodide, $(Bu_4N)HgI_3$, instead of the analogous chloride or bromide, $(Bu_4N)HgX_3$ (X = Cl, Br), resulted in the formation of the first compound in the ET—HgX_3^-—PhY system (X = Cl, Br, I; Y = Cl, Br) which does not involve the solvent. This may be connected with the increase in the size of the halogen atoms in the series Cl—Br—I. As a consequence, the $[Hg_2I_6]^{2-}$ anion has a dimeric structure, unlike the tetrameric structure of the $[Hg_4X_{12}(PhY)_2]^{4-}$ anions discovered in this system earlier. In turn, the changes in the composition and the structure of the anion result in changes in the ET packing in the conducting layer. In the semiconducting structure **1**, the ET cations have α''-type packing, while in the structures $(ET)_8[Hg_4X_{12}(PhY)_2]$ (X, Y = Cl, Br), with metallic conductivity, the ET cations are packed following the $(ET)_2ClO_4(TCE)_{0.5}$ structure[13], where TCE is 1,1,2-trichloroethane.

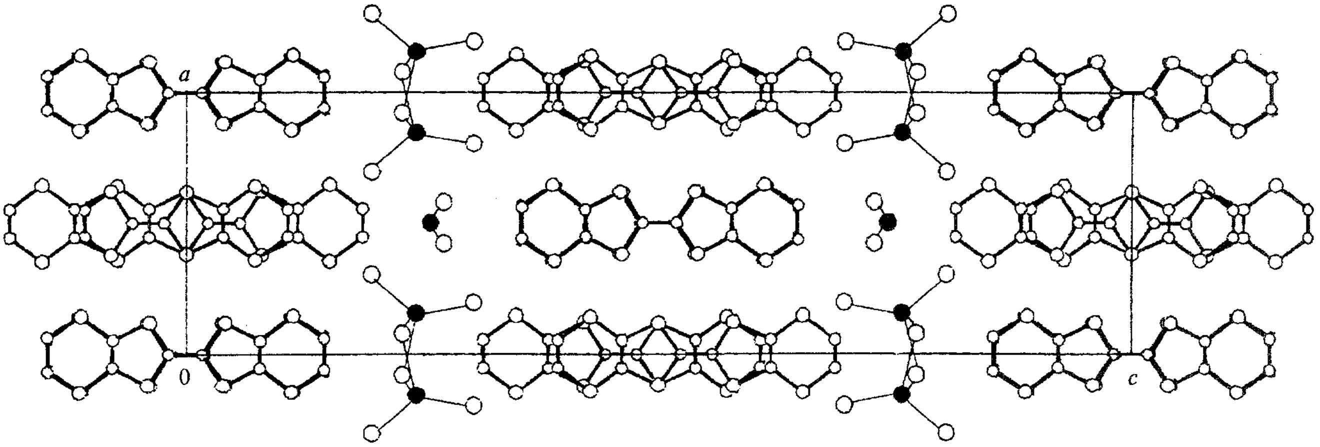

Fig. 4. Projection of structure **2** on the *ac* plane (*a* = 11.989(4), *b* = 8.430(3), *c* = 40.740(5) Å, γ = 111.08(2)°). Since the Hg atoms are statistically disordered in two positions with the same population density, μ = 0.5, the projection shows one of the two equally probable structures of the anionic layer for clarity.

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References

1. R. N. Lyubovskaya, T. V. Afanas'eva, O. A. D'yachenko, V. V. Gritsenko, Sh. G. Mkoyan, G. V. Shilov, R. B. Lyubovskii, V. N. Laukhin, M. K. Makova, A. G. Khomenko, and A. V. Zvarykina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2872 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2608 (Engl. Transl.)].
2. O. A. D'yachenko, V. V. Gritsenko, Sh. G. Mkoyan, G. V. Shilov, and L. O. Atovmyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2062 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1825 (Engl. Transl.)].
3. V. V. Gritsenko, O. A. D'yachenko, G. V. Shilov, R. N. Lyubovskaya, T. V. Afanas'eva, R. B. Lyubovskii, and M. K. Makova, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 894 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1992, **42**, 697 (Engl. Transl.)].
4. U. Walker and D. Stuart, *Acta Cryst.*, 1983, **A39**, 159.
5. G. M. Sheldrick, *SHELX-76, 86. Program for crystal structure determination*, University of Cambrige, England, 1976, 1986.
6. T. Mori, Y. Maruyama, H. Inokuchi, and G. Saito, *Solid State Comm.*, 1991, **78**, 49.
7. P. T. Beurskens, W. P. J. Bosman, and J. A. Cras, *J. Cryst. Mol. Struct.*, 1972, **2**, 183.
8. R. P. Shibaeva and V. F. Kaminskii, *Kristallografiya*, 1984, **29**, 606 [*Sov. Phys.-Crystallogr.*, 1984 (Engl. Transl.)].
9. J. Fabry and B. A. Maximov, *Acta Cryst.*, 1991, **C47**, 51.
10. D. A. Pears, J. F. Stoddart, J. Crosly, B. L. Allwood, and D. J. Williams, *Acta Cryst.*, 1986, **C42**, 804.
11. J. G. Contreras, G. V. Sequel, and W. Honle, *J. Mol. Struct.*, 1980, **68**, 1.
12. T. G. Takhirov, O. N. Krasochka, O. A. D'yachenko, L. O. Atovmyan, M. Z. Aldoshina, L. M. Goldenberg, R. N. Lyubovskaya, V. A. Merzhanov, and R. B. Lyubovskii, *Mol. Cryst. Liq. Cryst.*, 1990, **185**, 215.
13. H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, *J. Am. Chem. Soc.*, 1983, **105**, 297.

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