# New organic metals: radical cation salts of bis(ethylenedioxo)tetrathiafulvalene with halide mercurate anions

*E. I. Zhilyaeva,* S. A. Torunova, R. N. Lyubovskaya, and R. B. Lyubovskii*

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

Radical cation salts with halide mercurate anions were obtained by the electrochemical oxidation of bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF), and their conductivity was studied. The compounds $(BEDO\text{-}TTF)_4Hg_3X_8$ (X = Cl or Br), $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$, and $(BEDO\text{-}TTF)_2HgBr_3$ possess the conductivity of the metallic type down to helium temperatures.

**Key words:** bis(ethylenedioxo)tetrathiafulvalene, electrochemical oxidation; radical cation salts, halide mercurate anions; organic metals, conductivity.

In the synthesis of organic radical cation salts, even small changes in the cationic or anionic component of the salt affect substantially the structure and properties of the compounds. Recently it was found that mercury halides in the salts of bis(ethylenedithio)tetrathiafulvalene (ET) form anions of various compositions, structures, and charge states, which provides a variety of electroconducting properties of radical cation salts of ET with halide mercurate anions: from semiconducting to superconducting properties (see Ref. 1 and works cited therein). Therefore, it was of interest to study the effect of the substitution of ET in the cationic component for bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF), analog of ET containing O atoms in the six-membered cycles, on the properties of radical cation salts with halide mercurate anions.

Several known BEDO-TTF radical cation salts are characterized by the conductivity of the metallic type.[2–4] The compounds $(BEDO\text{-}TTF)_3Cu_2(CNS)_3$ [5] and $(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$ [6–8] undergo the transition to the superconducting state, and the structures of BEDO-TTF salts differ substantially from ET ones with the corresponding anions.[2,3,5,7,8]

In this work we report on the synthesis of new BEDO-TTF radical cation salts with halide mercurate anions and the study of their conductivity.

## Experimental

All radical cation salts were obtained by the electrochemical oxidation of BEDO-TTF solutions in 1,2-dichloroethane using $Bu_4NHgX_3$ or $Bu_4NHgX_3$—$HgX_2$ system as supporting electrolytes at room temperature. The salts were formed on a Pt anode as single crystals (Table 1). The electroconductivity of crystals was measured by the standard d.c. four-probe method.

The composition of iodo- and bromomercurates determined by the elemental analysis was confirmed by electron probe microanalysis.

## Results and Discussion

Preparation of BEDO-TTF salts, which possess conductivity of the metallic type, using KX—crown ether—$HgX_2$ mixtures (X = Cl, Br, I) as supporting electrolytes has been previously reported.[4] However, the composition and structure of the products have not been determined. We used the supporting electrolytes of the composition $Bu_4NHgX_3$ (X = Cl, Br, I) obtained by the procedure described previously.[9] The electrochemical oxidation of BEDO-TTF in the presence of these supporting electrolytes at the current densities of 2—4 μA $cm^{-2}$ and 293 K made it possible to isolate compounds of the composition $(BEDO\text{-}TTF)_2HgX_3$ in the individual state formed as very thin needles. In the case of ET, tribromo- and trichloromercurates of similar stoichiometry always contain a solvent,[10,11] and only the composition of the ET salt with the $HgI_3^-$ anion (see Ref. 12) completely coincides with the compositions of the BEDO-TTF salts obtained.

To synthesize the BEDO-TTF salts with the $[Hg_3X_8]^{2-}$ anions, $HgX_2$ was added to the supporting electrolyte $Bu_4NHgX_3$. The complex formation occurring here cause the presence of different anions in the solution. It should be emphasized that when the solution contains a set of anions, crystals of the radical cation salts that possess a high electroconductivity, grow on the anode upon electrocrystallization, and conducting compounds of differing composition can be formed simultaneously. The salts of stoichiometric and nonstoichiometric composition, $(ET)_4Hg_3X_8$, [13,14] $(ET)_4Hg_{2.89}Br_8$, [15] and $(ET)_4Hg_{2.78}Cl_8$,[16] as a rule, in a mixture with the salts

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1167—1170, May, 1996.

**Table 1.** Conditions for the synthesis of halide mercurates of BEDO-TTF

| Concentration /mmol $L^{-1}$ | | | $T$ | $j^*$ | Product | Found / Calculated (%) | |
|---|---|---|---|---|---|---|---|
| BEDO-TTF | $Bu_4NHgX_3$ (X) | $HgX_2$ | /°C | /μA $cm^{-2}$ | (form of crystals) | C | H |
| 2.5 | 3.0 (I) | — | ~20 | 4 | $(BEDO\text{-}TTF)_2HgI_3$ (needles) | 20.07<br>19.71 | 1.32<br>1.31 |
| 1.7 | 1.5 (Br) | — | ~20 | 2 | $(BEDO\text{-}TTF)_2HgBr_3$ (needles) | 22.59<br>22.20 | 2.09<br>1.48 |
| 3.0 | 2.0 (Cl) | — | ~20 | 2 | $(BEDO\text{-}TTF)_2HgCl_3$ (fibers) | 25.42<br>25.35 | 1.70<br>1.70 |
| 3.3 | 2.0 (I) | 4.00 | 23 | 2 | $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ (plates) | 15.81<br>15.45 | 1.25<br>1.02 |
| 2.5 | 1.5 (Br) | 0.75 | 13 | 2 | $(BEDO\text{-}TTF)_4Hg_3Br_8$ (plates) | 19.51<br>19.04 | 1.06<br>1.28 |
| 3.0 | 1.7 (Cl) | 0.85 | ~20 | 60 | $(BEDO\text{-}TTF)_4Hg_3Cl_8$ (plates) | 22.03<br>22.10 | 1.53<br>1.48 |

* Current density.

$(ET)_2HgX_3 \cdot nS$ were obtained from ET under these conditions. To prepare individual compounds of BEDO-TTF, we studied the phase composition of the electrocrystallization products depending on the ratios of the components of the supporting electrolyte, $Bu_4NHgX_3$ and $HgX_2$. The variation of $Bu_4NHgBr_3$ : $HgBr_2$ molar ratio from 1.0 : 0.2 to 1.0 : 0.5 made it possible to establish that single crystals only of the composition $(BEDO\text{-}TTF)_4Hg_3Br_8$ are formed at current densities from 2 to 4 μA $cm^{-2}$ and a ratio of the components of 1.0 : 0.5. A decrease in the amount of $HgBr_2$ always results in the formation of a mixture of $(BEDO\text{-}TTF)_2HgBr_3$ and $(BEDO\text{-}TTF)_4Hg_3Br_8$.

In the case of $Bu_4NHgI_3$ and $HgI_2$, a much greater amount of $HgI_2$ is required to prevent the formation of the salt $(BEDO\text{-}TTF)_2HgI_3$. When the current density is equal to ~4 μA $cm^{-2}$ and $Bu_4NHgI_3$ : $HgI_2$ = 1 : 2 (mol/mol), the growth of $(BEDO\text{-}TTF)_2HgI_3$ crystals completely ceases, and only $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ crystals are formed on the anode. It can be assumed that the $[Hg_7I_{18}]^{4-}$ anion is formed due to the coordination of two $[Hg_3I_8]^{2-}$ anions with the $HgI_2$ molecule. It is likely that this is the reason for the necessity of considerably greater amounts of $HgI_2$ than those of $HgBr_2$.

When the chloromercurate system $Bu_4NHgCl_3$—$HgCl_2$ is used, BEDO-TTF is gradually chemically oxidized by mercuric chloride in the solution. The precipitate formed in the bulk of the electrochemical cell (not on the anode) at the molar ratio $Bu_4NHgCl_3$ : $HgCl_2$ = 1 : 2 has the composition of $(BEDO\text{-}TTF)_4Hg_5Cl_{12}$. To increase the rate of the electrochemical oxidation of BEDO-TTF compared to that of the chemical oxidation, we increased the current density (~60 μA $cm^{-2}$) at the ratio $Bu_4NHgCl_3$ : $HgCl_2$ = 1.0 : 0.5 (mol/mol) and obtained only $(BEDO\text{-}TTF)_4Hg_3Cl_8$ crystals on the anode.

Thus, varying the composition of the electrolyte and current density, we succeeded in isolating the radical cation salts of BEDO-TTF with the anions $[HgX_3]^-$, $[Hg_3X_8]^{2-}$, and $[Hg_{3.5}I_9]^{2-}$.

**Electroconductivity.** The conductivity (σ) of the $(BEDO\text{-}TTF)_2HgBr_3$ salt at 293 K is 500—700 $Ohm^{-1}$ $cm^{-1}$, and the σ values of the other compounds range from 10 to 200 $Ohm^{-1}$ $cm^{-1}$. The attempts to measure the electroconductivity of $(BEDO\text{-}TTF)_2HgCl_3$ crystals, which are thinnest fibers, were unsuccessful.

The temperature dependences of the resistance of single crystals of the salts obtained were studied in the range from 293 K to helium temperatures. Many researchers mention that the BEDO-TTF salts are characterized by the appearance of jumps on the resistance curves (so-called cracks that are likely caused by internal strains in crystals) as the temperature decreases.[3,4,8] Similar phenomena were also observed for halide mercurate salts of BEDO-TTF.

The compound $(BEDO\text{-}TTF)_2HgI_3$ manifests the metallic character of the temperature dependence of the

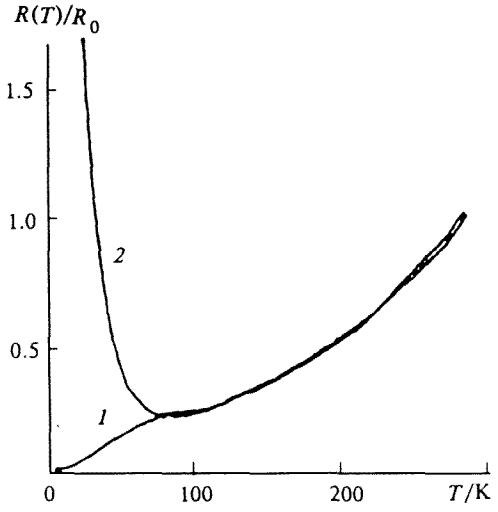


**Fig. 1.** Temperature dependences of the relative resistance for $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ (*1*) and $(BEDO\text{-}TTF)_2HgI_3$ (*2*).

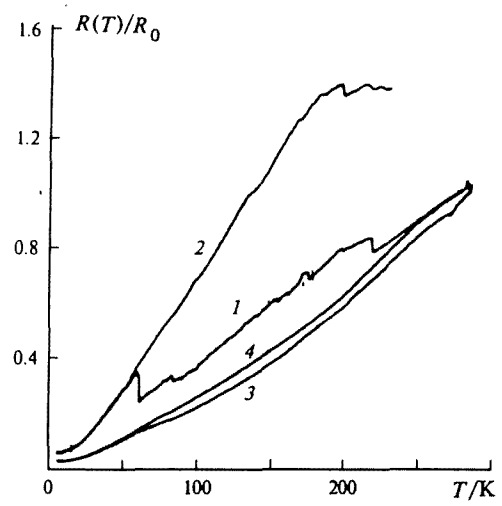


**Fig. 2.** Temperature dependence of the relative resistance for $(BEDO\text{-}TTF)_4Hg_3Cl_8$: *1*, cooling; *2*, warming; *3*, cooling at $p$ = 0.5 kbar; *4*, warming at $p$ = 0.5 kbar.

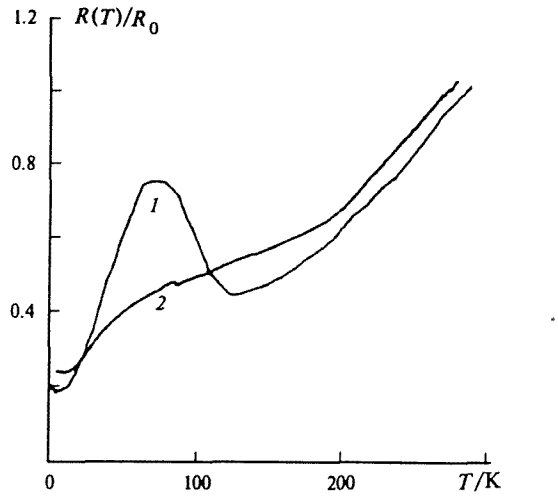


**Fig. 3.** Temperature dependence of the relative resistance for $(BEDO\text{-}TTF)_4Hg_3Br_8$: *1*, at atmospheric pressure; *2*, at $p$ = 0.5 kbar.

resistance and at ~75 K undergoes the metal—insulator transition (Fig. 1, curve *2*). The ET salt of similar stoichiometry is a semiconductor.[12]

No dielectrization occurs in the salts of the composition $(BEDO\text{-}TTF)_4Hg_3X_8$ (X = Cl or Br) and $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ as the temperature decreases down to 1.5 K (Figs. 1—3, curves *1*). The values of the decrease in the resistance at 5 K ($R_{297}/R_5$) are 20, 65—280, and 5 for X = Cl, I, and Br, respectively.

The curves of the temperature dependences for $(BEDO\text{-}TTF)_2HgI_3$ and $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ coincide completely in the range of 297—75 K. The divergence of the curves at $T$ < 75 K is likely associated with the different effects of the anion on the conducting layers. The temperature dependences of the resistance of the salts with the anions $[Hg_3Cl_8]^{2-}$ and $[Hg_{3.5}I_9]^{2-}$ are very similar (see Figs. 1 and 2, curves *1*). Two regions can be distinguished on these curves: the region with the smooth decrease in the resistance at the temperatures from 293 to 60 K (X = Cl) or 75 K (X = I) and the low-temperature region, where the decrease in the resistance accelerates and then reaches a flattened minimum at ~5 K. The curve of the temperature dependence of octabromomercurate (see Fig. 3, curve *1*) is distinguished by the appearance of a maximum in the range of ~75 K. At low pressure (~0.5 kbar), the maximum is completely suppressed (see Fig. 3, curve *2*), and the temperature dependence for bromomercurate becomes similar to those for chloro- and iodomercurates. Thus, in the temperature range from 293 to 1.5 K, the salts $(BEDO\text{-}TTF)_4Hg_3X_8$ (X = Cl, Br) and $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ are metals. In the ET salts of similar stoichiometry, the metallic state is less stable with respect to both the transitions of the metal—insulator type ($T_{M-I}$ = 262 and 20 K in the salts $(ET)_4Hg_3X_8$ at X = I and Br, respectively[13,14]) and the metal—superconductor transitions ($T_c$ = 4.3 K for $(ET)_4Hg_{2.89}Br_8$ [15] and $T_c$ = 1.8 K at $p$ = 12 kbar for $(ET)_4Hg_{2.78}Cl_8$ [16]).

It is noteworthy that hysteresis, the reasons for which are not quite clear, was observed in all measurements of the $(BEDO\text{-}TTF)_4Hg_3X_8$ and $(BEDO\text{-}TTF)_4Hg_{3.5}I_9$ salts. When the samples are heated from helium temperatures up to 293 K, the patterns of the resistance curves coincide completely in the range below 60 K (X = Cl) or 75 K (X = Br, I). The low-temperature phase retains as the temperature increases further, and the heating curves differ substantially from the cooling ones, as it is seen in Fig. 2 (curve *2*) for chloromercurate. When the pressure (0.5 kbar) is applied, the divergence in the cooling and heating cycles persists at temperatures higher than 60 K (see Fig. 2, curves *3* and *4*).

These results show that the metallic state in BEDO-TTF halide mercurates in the temperature range from 293 to 1.5 K is more stable than in the case of halide mercurates of ET.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-09950a), the Scientific Council on HTSC ("Poisk" 93-030), and the International Science Foundation and the Government of the Russian Federation (Grants REI 000, REI 300, and JB3 100).

## References

1. R. N. Lyubovskaya, O. A. Dyachenko, and R. B. Lyubovskii, *Synth. Met.*, 1993, **55—57**, 2899.
2. F. Wudl, H. Yamochi, T. Suzuki, H. Isotalo, C. Fite,

H. Kasmai, K. Liou, G. Srdanov, P. Coppens, K. Maly, and A. Frost-Jensen, *J. Am. Chem. Soc.*, 1990, **112**, 2461.
3. M. A. Beno, H. H. Wang, K. D. Carlson, A. M. Kini, G. M. Frankenbach, J. R. Ferraro, N. Larson, G. D. McCabe, J. Thompson, C. Purnama, M. Vashon, and J. M. Williams, *Mol. Cryst., Liq. Cryst.*, 1990, **181**, 145.
4. H. Yamochi, T. Nakamura, G. Saito, T. Kikuchi, S. Sato, K. Nozawa, M. Kinoshita, T. Sugano, and F. Wudl, *Synth. Met.*, 1991, **41—43**, 1741.
5. M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Tompson, J. M. Williams, J. Ren, and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 1599.
6. S. Kahlich, D. Schweitzer, I. Heinen, Song En Lan, B. Nuber, H. J. Keller, K. Winzer, and H. W. Helberg, *Solid State Commun.*, 1991, **80**, 191.
7. D. Schweitzer, S. Kahlich, I. Heinen, Song En Lan, B. Nuber, H. J. Keller, K. Winzer, and H. W. Helberg, *Synth. Met.*, 1993, **56**, 2827.
8. V. V. Laukhin, L. I. Buravov, A. G. Khomenko, N. D. Kushch, A. I. Schegolev, E. B. Yagubskii, L. P. Rosenberg, and R. P. Shibaeva, *Synth. Met.*, 1993, **56**, 2877.
9. P. L. Goggin, P. King, D. M. McEwan, G. E. Tayler, P. Woodward, and M. Sandstrom, *J. Chem. Soc., Dalton Trans.*, 1982, 875.
10. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo, in *Organic Superconductors (Including Fullerenes)*, Ed. R. N. Grimes, Englwood Cliffs—Prentice Hall, New Jersey, 1992, 55.
11. 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.)].
12. O. A. D'yachenko, V. V. Gritsenko, G. V. Shilov, R. N. Lyubovskaya, and R. B. Lyubovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1240 [*Russ. Chem. Bull.*, 1994, **43**, 1175 (Engl. Transl.)].
13. T. G. Takhirov, O. N. Krasochka, O. A. Dyachenko, 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.
14. S. V. Konovalikhin, O. A. Dyachenko, and N. D. Kushch, in *Abstrs. Intern. Conf. on Sci. and Technol. of Synth. Met.*, Seoul (Korea), 1994, 140.
15. R. N. Lyubovskaya, E. I. Zhilyaeva, S. I. Pesotskii, R. B. Lyubovskii, L. O. Atovmyan, O. A. D'yachenko, and T. G. Takhirov, *Pis'ma v ZhETF*, 1987, **46**, 149 [*JETP Lett.*, 1987, **46**, 189 (Engl. Transl.)].
16. M. Z. Aldoshina, L. M. Goldenberg, E. I. Zhilyaeva, R. N. Lyubovskaya, T. G. Takhirov, O. A. Dyachenko, L. O. Atovmyan, and R. B. Lyubovskii, *Mater. Sci.*, 1988, **14**, 45.

*Received October 6, 1995;*
*in revised form November 27, 1995*