Russian Chemical Bulletin, International Edition, Vol. 52, No. 2, pp. 375—379, February, 2003

Structures and conductivities of isostructural synthetic metals $(DOET)_4[Hg_2Cl_6]$ and $(DOET)_4[Hg_2Br_6]$

O. A. D´yachenko,[a] A. A. Bardin,[a]* A. I. Kotov,[a] G. V. Shilov,[a] V. V. Gritsenko,[a] L. I. Buravov,[a] and M. Mizuno[b]

[a]Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: andrew@icp.ac.ru
[b]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaruki 305, Japan
Fax: +81 3 (298) 54 4709

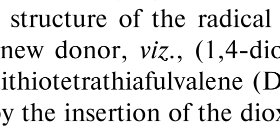
The structures of organic metals $(DOET)_4[Hg_2Cl_6]$ (**1**) and $(DOET)_4[Hg_2Br_6]$ (**2**), where DOET is (1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene, were established by X-ray diffraction analysis. Compounds **1** and **2** are isostructural, and their crystals have layered structures. The conducting layers formed by the stacked $DOET^{1/2+}$ cations alternate with the layers of the $[Hg_2X_6]^{2-}$ anions (X = Cl, Br). The temperature dependence of the conductivity of salt **1** shows a metallic character in the range of 300—4 K. Compound **2** undergoes the metal—semiconductor phase transition (T_{M-I}) at 100 K.

Key words: organic metals, DOET, mercury halides, intermolecular contacts, packing mode.

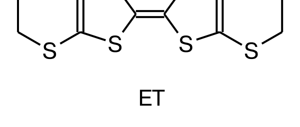
Radical cation salts based on planar π-conjugated organic electron donors attract considerable attention, because some of these compounds possess metallic and superconducting properties.[1,2]

Bis(ethylenedithio)tetrathiafulvalene (ET) is a donor most commonly used for the preparation of organic metals. In crystals, the radical cations ET form conducting layers alternating with layers of counterions. The packing mode of ET in the layer correlates with the conductivity of organic conductors.[3]

With the aim of studying the influence of the steric factors on the structure of the radical cation layer, we synthesized a new donor, *viz.*, (1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene (DOET),[4] which is ET modified by the insertion of the dioxane ring located symmetrically with respect to the long molecular axis.



ET



DOET

Earlier, a series of radical cation salts with different anions have been synthesized based on DOET, *viz.*, $(DOET)_2ReO_4$,[5] $(DOET)_2BF_4$,[6] *etc.* These salts belong to layered compounds exhibiting the quasi-2D conductivity. It appeared that DOET involved in salts tends to form β-like packings of the conducting layers. This packing mode has been found earlier in the first ET-based organic superconductor, *viz.*, in β-$(ET)_2I_3$, under atmospheric pressure.[7]

In the present study, we report the synthesis, conducting properties, and results of X-ray diffraction analysis of two isostructural organic metals, *viz.*, $(DOET)_4[Hg_2Cl_6]$ (**1**) and $(DOET)_4[Hg_2Br_6]$ (**2**).

Experimental

Synthesis. Crystals of compounds **1** and **2** were prepared by electrochemical oxidation of DOET in solutions of mercury salts. A solution of DOET (10 mg, $1.1 \cdot 10^{-3}$ mol L^{-1}), $[(Ph_3P)_2N]HgCl_3$ (245 mg, $1.45 \cdot 10^{-2}$ mol L^{-1}), and $HgCl_2$ (5 mg, $9.2 \cdot 10^{-4}$ mol $^{-1}$) (for **1**) or $(Bu_4N)HgBr_3$ (200 mg, $1.46 \cdot 10^{-2}$ mol L^{-1}) and $HgBr_2$ (7 mg, $9.7 \cdot 10^{-4}$ mol L^{-1}) (for **2**) in chlorobenzene (20 mL) with an additive of anhydrous EtOH (10%) was subjected to electrochemical anodic oxidation at constant current density of 1 μA cm^{-2} and 25 °C. Single crystals of **1** and **2** suitable for X-ray diffraction study and conductivity measurements were produced at a Pt anode during two weeks.

Conductivity. The in the *ac*-plane conductivities of the crystals of **1** and **2** were measured in the range of 300—4 K by a standard four-electrode method. At room temperature, $\sigma_{\|room}$ are 66 (**1**) and 20 S cm^{-1} (**2**). The temperature dependence of the conductivity shows a metallic character (Fig. 1).

X-ray diffraction analysis. The principal crystallographic characteristics of $(DOET)_4[Hg_2Cl_6]$: $C_{48}H_{40}Cl_6Hg_2O_8S_{32}$, M = 2384.85, triclinic, a = 12.637(3) Å, b = 18.779(3) Å,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 359—363, February, 2003.

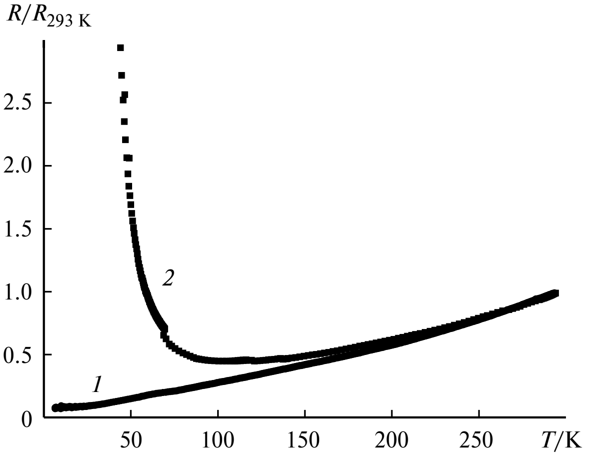


Fig. 1. Temperature dependence of the relative resistance of salts **1** (*1*) and **2** (*2*).

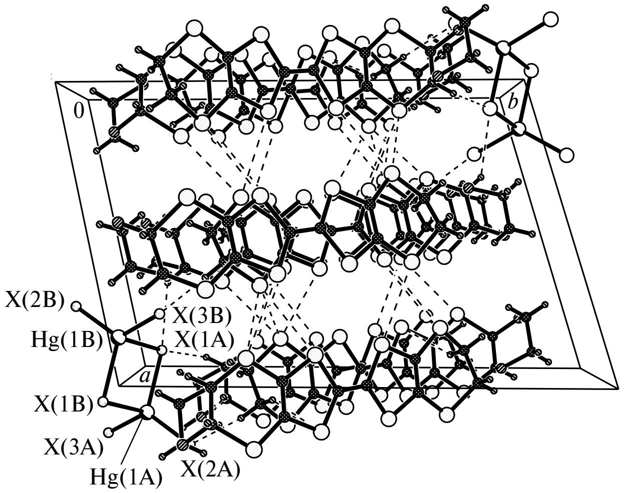


Fig. 2. Crystal structure of $(\mathrm{DOET})_4[\mathrm{Hg_2X_6}]$ (X = Cl (**1**), Br (**2**)).

c = 8.867(4) Å, α = 86.00(2)°, β = 72.62(3)°, γ = 75.26(2)°, V = 1942.2(9) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 2.039 g cm^{-3}, F(000) = 1166. The X-ray diffraction data were collected from a thin rectangular platelet-like crystal of dimensions 0.6×0.5×0.1 mm on an automated four-circle KUMA DIFFRACTION KM-4 diffractometer ($\omega/2\theta$ scan technique, graphite monochromator, CuKα radiation, $(2\theta)_{\max}$ = 160.94°). A total of 8009 independent reflections were measured of which 5691 reflections were with $F > 4\sigma(F)$. The analytical absorption correction[8] was applied using the crystal habit (μ(CuKα) = 17.34 mm^{-1}). The structure was solved by direct methods followed by calculations of Fourier maps with the use of the SHELX-86 and SHELX-93[9] program packages. The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method; 15 of 20 hydrogen atoms were revealed from difference Fourier maps and refined isotropically. The positions of the remaining hydrogen atoms were calculated geometrically. The final R factors were as follows: R = 0.0556 and R_ω = 0.1847 for reflections with $F > 4\sigma(F)$.

The principal crystallographic characteristics of $(\mathrm{DOET})_4[\mathrm{Hg_2Br_6}]$: $\mathrm{C_{48}H_{40}Br_6Hg_2O_8S_{32}}$, M = 2651.56, triclinic, a = 12.819(4) Å, b = 18.744(7) Å, c = 8.950(2) Å, α = 86.64(3)°, β = 72.92(3)°, γ = 75.27(3)°, V = 1987.7(11) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 2.214 g cm^{-3}, F(000) = 1274. The X-ray diffraction data were collected from a rectangular plate-like crystal of dimensions 0.8×0.7×0.4 mm on an automated four-circle KUMA DIFFRACTION KM-4 diffractometer ($\omega/2\theta$ scan technique, graphite monochromator, MoKα radiation, $(2\theta)_{\max}$ = 134.10°). A total of 7068 independent reflections were measured of which 3369 reflections were with $F > 4\sigma(F)$. Absorption was ignored (μ(MoKα) = 3.88 mm^{-1}). The structure was solved by direct methods followed by calculations of Fourier maps with the use of the SHELX-86 and SHELX-93[9] program packages. The nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. The positions of all hydrogen atoms were calculated geometrically. The final R factors were as follows: R = 0.0607 and R_ω = 0.1890 for reflections with $F > 4\sigma(F)$.

All calculations were carried out with the use of the WinGX crystallographic program package.[10]

Results and discussion

Compounds **1** and **2** are isostructural. The replacement of the Cl atoms by Br in the anionic portion of the $(\mathrm{DOET})_4[\mathrm{Hg_2X_6}]$ compound (X = Cl (**1**) or Br (**2**)) leads to an increase in the unit cell volume by 45 Å with retention of the packing mode of the radical cations in the conducting layer.

The crystal structures of **1** and **2** (Fig. 2) are built of the alternating organic and inorganic layers typical of ET salts.[11] The organic layers contain two types of crystallographically independent DOET radical cations (**A** and **B**) with the average formal charge +1/2 (Fig. 3). The inorganic layers are composed of the $\mathrm{HgX_3}^-$ anions (X = Cl (**1**) or Br (**2**)) and alternate with the organic layers along the b axis of the crystal.

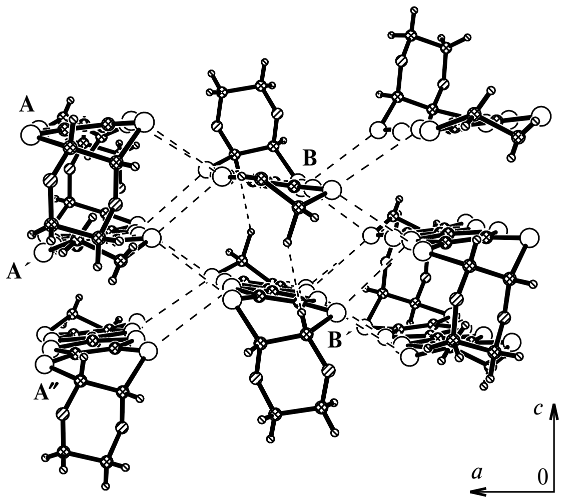


Fig. 3. Radical cation layer of salt **1** projected onto the *ac* plane (crystallographically equivalent molecules are denoted by primed labels).

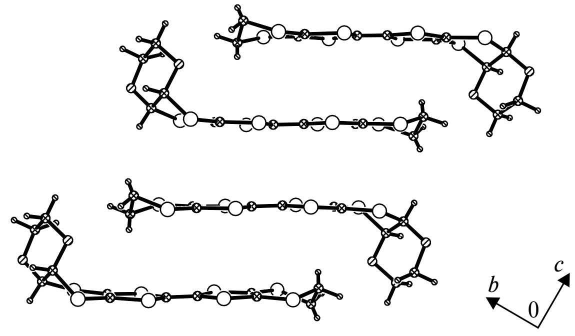


Fig. 4. Stacks of the $DOET^{1/2+}$ radical cations in salts **1** and **2**.

In the inorganic layers of salts **1** and **2**, the trigonal HgX_3^- anions are linked in the $[Hg_2X_6]^{2-}$ dimers through the directed Hg(1A)...X(1B) and Hg(1B)...X(1A) coordination bonds (2.809(3) Å for **1** and 2.931(2) Å for **2**) (see Fig. 2). The mercury atoms in the anions have a distorted tetrahedral configuration with the Hg(1) atom deviating from the Cl(1)—Cl(2)—Cl(3) plane in **1** by 0.235 Å and from the Br(1)—Br(2)—Br(3) plane in **2** by 0.266 Å. The Hg—Cl bond lengths in **1** are in the range of 2.360(3)—2.518(3) Å. The Hg—Br bond lengths in **2** are in the range of 2.487(2)—2.622(2) Å. The Cl—Hg—Cl and Br—Hg—Br bond angles in **1** and **2**, respectively, are in the ranges of 109.1(5)°—129.0(6)° and 110.4(7)°—127.4(7)° (Table 1).

Table 1. Principal bond lengths and bond angles in the anions of compounds **1** (X = Cl) and **2** (X = Br)

Parameter	**1**	**2**
Bond	d/Å	
Hg(1A)—X(1A)	2.518(3)	2.622(2)
Hg(1A)—X(2A)	2.403(3)	2.513(2)
Hg(1A)—X(3A)	2.360(3)	2.487(2)
Hg(1A)—X(1B)	2.809(3)	2.931(2)
Bond angle	ω/deg	
X(1A)—Hg(1A)—X(2A)	109.1(5)	110.4(7)
X(1A)—Hg(1A)—X(3A)	119.5(5)	118.9(8)
X(2A)—Hg(1A)—X(3A)	129.0(6)	127.4(7)

In the radical cation layers, the $DOET^{1/2+}$ cations are grouped in stacks, each stack being formed by either **A** or **B** molecules. The stacks are extended along the *c* axis and form an angle of 35° with the normal to the DOET plane. The $DOET^{1/2+}$ cations in the organic layers are linked in head-to-tail dimers (Fig. 4). In the dimers, the radical

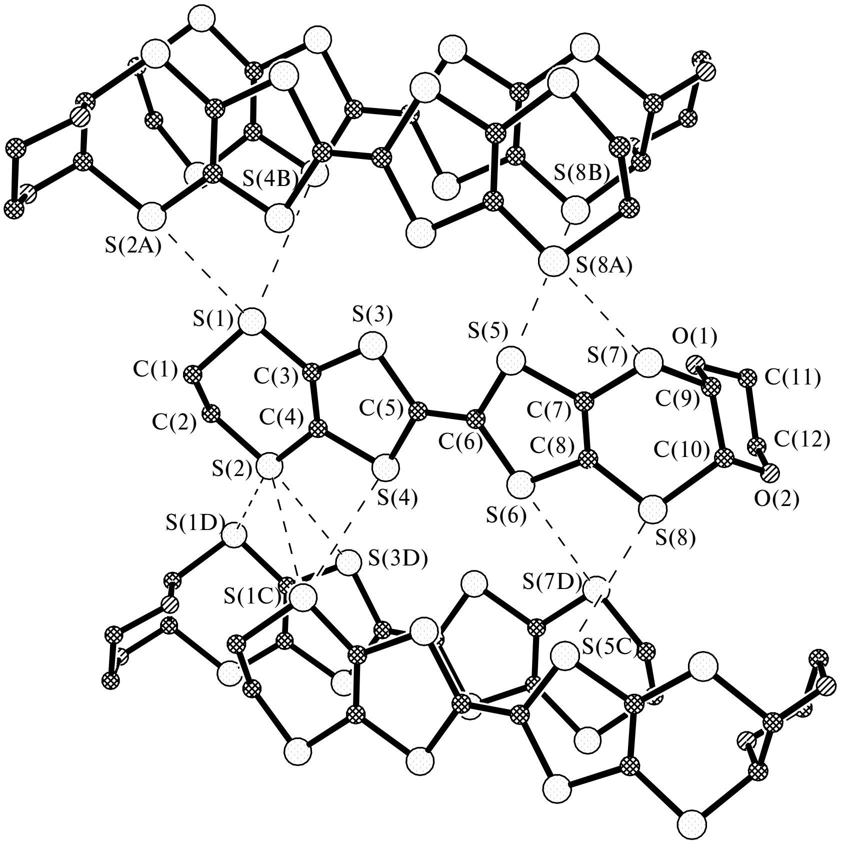


Fig. 5. Environment of the $DOET^{1/2+}$ radical cation (**A**) in the layer in the structure of **1**. Shortened intermolecular S...S contacts are indicated by dashed lines.

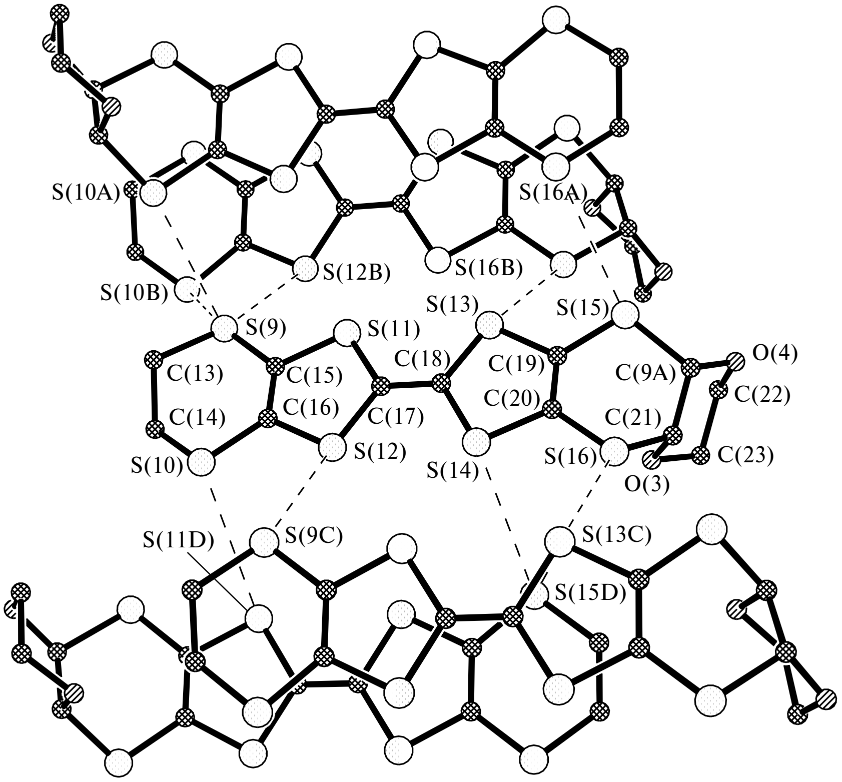


Fig. 6. Environment of the DOET$^{1/2+}$ radical cation (**B**) in the layer in the structure of **1**.

cations are shifted with respect to each other by 4 Å along the long molecular axis due to the steric effect of the terminal dioxane fragments of the radical cations. The dioxane rings of the radical cations (Fig. 5, the C(9)—C(12), O(1), and O(2) atoms for **A**) adopt a chair conformation and are located virtually perpendicular to the plane of the central TTF fragment of the molecule (see Fig. 5). The dimers are shifted with respect to each other by 1 Å. In isomers **1** and **2**, the distances between the DOET$^{1/2+}$ cations in the dimers are 3.501 and 3.762 Å, respectively. The distances between the dimers are 3.682 and 3.666 Å in **1** and **2**, respectively. In the organic layers, the stacks are linked by numerous shortened intermolecular S...S contacts (Table 2, Figs. 5 and 6).

The interstack S...S contacts in radical cation salts **1** and **2** give rise to two-dimensional conductivity networks. The contacts are formed primarily through the peripheral S(1), S(2), S(7), and S(8) atoms. In our opinion, this is associated with the fact that these atoms are more sterically accessible. In the organic layers, each DOET$^{1/2+}$ cation is linked to four radical cations from the adjacent stacks through shortened contacts (ten S...S contacts in **1** and nine S...S contacts in **2**; see Figs. 5 and 6). As can be seen from Table 2, the intermolecular S...S contacts in **2** are longer than those in **1**. The average bond length of these contacts in **2** is 0.039 Å larger than that in **1**.

The oxygen atoms of the dioxane ring of DOET$^{1/2+}$ do not form shortened S...O and O...O contacts and are not involved in the conductivity network. Apparently, the dioxane fragment hinders the formation of a two-dimensional conductivity network, because the size of the dioxane ring is such that it makes impossible the uniform arrangement of the stacks of DOET$^{1/2+}$, which would be optimum for the formation of S...S contacts. In spite of the steric factor, salt **1** shows a metallic temperature de-

Table 2. Lengths of the shortened intermolecular S...S contacts in compounds **1** and **2**

Contact	*d*/Å	
	1	**2**
S(1)—S(2A)	3.524	3.550
S(1)—S(4B)	3.602	3.653
S(2)—S(1C)	3.449	3.524
S(2)—S(1D)	3.585	3.651
S(2)—S(3D)	3.484	3.549
S(4)—S(1C)	3.371	3.407
S(5)—S(8B)	3.547	3.652
S(6)—S(7D)	3.635	3.655
S(7)—S(8A)	3.420	3.432
S(8)—S(5C)	3.631	—
Σ(S...S)/*n*	3.525	3.564
S(9)—S(10A)	3.420	3.432
S(9)—S(10B)	3.449	3.549
S(9)—S(12B)	3.371	3.407
S(10)—S(11D)	3.635	3.655
S(12)—S(9C)	3.602	3.653
S(13)—S(16B)	3.631	—
S(14)—S(15D)	3.484	3.524
S(15)—S(16A)	3.524	3.550
S(16)—S(13C)	3.547	3.652
S(16)—S(15D)	3.585	3.651
Σ(S...S)/*n*	3.525	3.564

pendence of the conductivity throughout the temperature range under study (300—4 K). The data obtained in our study agree with the results of quantum-chemical calculations from which is follows that the motion of conductivity electrons in the crystal is associated with the central fragments of tetrathiafulvalene (TTF) possessing the highest spin density on radical cations.[12]

The dihedral angle between the planes of the radical cations (planes pass through all atoms, except for the dioxane fragment) belonging to adjacent stacks are 14.3° and 12.4° in salts **1** and **2**, respectively. In β-$(ET)_2I_3$, the radical cations are parallel to each other.[7] In α-$(ET)_2I_3$, the corresponding angles are 53° and 70°.[13] The previously unknown packing mode of the donor molecules in salts **1** and **2** is intermediate between the α and β types of the donor environment.

The conductivities of salts **1** and **2** correlate with the lengths of the intermolecular S...S contacts. Salt **1** exhibits better conducting properties than **2** (see Fig. 1). An increase in the conductivity with decreasing size of the anion in the isostructural series and, as a consequence, shortening of the S...S contacts ("isostructural contraction") have been observed earlier in $(ET)_8[Hg_4Cl_{12}(PhCl)_2]$ [14] and $(ET)_8[Hg_4Br_{12}(PhCl)_2]$.[15] The chlorobenzene molecules in salts **1** and **2**, unlike those in ET salts, are not involved in the inorganic layers, which is, most likely, to be associated with the steric effect of the dioxane ring deviating from the organic layer.

The electronic structure of the crystal of salt **2** differs from that of isostructural salt **1** due to elongation of the corresponding shortened S...S contacts and an increase in the interplanar distances in the stacks of the radical cations. Apparently, this is the reason for the occurrence of the metal—semiconductor phase transition in salt **2** at 100 K, whereas salt **1** is a stable metal. In our opinion, DOET is a promising electron donor for the preparation of highly conducting organic phases. The dioxane ring in the DOET molecule allows one to modify the packing mode of the donor molecules in the structures, *i.e.*, to perform a targeted search for highly conducting compounds.

We thank E. B. Yagubskii for helpful discussion and valuable advice.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32809) and INTAS (Grant 2001-2212).

References

1. R. N. Lyubovskaya, R. B. Lubovskii, R. P. Shibaeva, M. Z. Aldoshina, L. M. Goldenberg, L. P. Rozenberg, M. L. Khidekel, and Yu. F. Shulpyakov, *JETP Lett.*, 1985, **42**, 468.
2. R. N. Lyubovskaya, E. I. Zhilyaeva, S. I. Pesotskii, R. B. Lubovskii, L. O. Atovmyan, O. A. Dyachenko, and T. G. Takhirov, *JETP Lett.*, 1987, **46**, 188.
3. V. V. Gritsenko, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Chernogolovka, Moscow Region, 1994, 163 pp. (in Russian).
4. A. I. Kotov, L. I. Buravov, S. V. Konovalikhin, O. A. Dyachenko, E. B. Yagubskii, I. Malfant, T. Courcet, P. Cassoux, J. Akimoto, K. Honda, and M. Mizuno, *Synth. Met.*, 1999, **102**, 1630.
5. V. V. Gritsenko, O. A. D´yachenko, A. I. Kotov, L. I. Buravov, and M. Mizuno, *Koord. Khim.,* 2001, **27**, 432 [*Russ. J. Coord. Chem.,* 2001, **27** (Engl. Transl.)].
6. J. Yamada, S. Tanaka, H. Anzai, T. Sato, H. Nishikawa, I. Ikemoto, and K. Kikuchi, *J. Mater. Chem.*, 1997, **7**, 1311.
7. E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Konovich, M. V. Kartsovnic, A. V. Zvarykina, and L. I. Buravov, *JETP Lett.*, 1984, **39**, 12.
8. J. de Meulenaar and H. Tompa, *Acta Crystallogr.*, 1965, **A19**, 1014.
9. G. M. Sheldrick, *SHELX86, SHELXL93, Program for the Solution (Refinement) of Crystal Structure*, Göttingen University, Göttingen (Germany), 1986, 1993.
10. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
11. T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, Springer-Verlag, Heidelberg, 1998, 528 pp.
12. S. S. Parkin, E. M. Engler, V. J. Lee, and R. R. Schumaker, *Mol. Cryst. Liq. Cryst.*, 1985, **119**, 375.
13. I. Hennig, K. Bender, D. Schweitzer, K. Diez, H. Endrez, H. J. Keller, A. Gleiz, and H. W. Helberg, *Mol. Cryst. Liq. Cryst.*, 1985, **119**, 337.
14. O. A. D´yachenko, V. V. Gritsenko, Sh. G. Mkoyan, G. V. Shilov, and A. O. Atovmyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2062 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*,1991, **40**, 1825 (Engl. Transl.)].
15. O. A. D´yachenko, V. V. Gritsenko, G. V. Shilov, N. P. Karpova, and R. N. Lyubovskaya, *Koord. Khim.,* 1997, **23**, 655 [*Russ. J. Coord. Chem.,* 1997, **23** (Engl. Transl.)].

Received June 20, 2002