Synthesis, structures, and conductivities of salts (BEDT-TTF)[9,9′(12′)-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$] and (TTF)[9,9′,12,12′-I_4-3,3′-Co(1,2-$C_2B_9H_9$)$_2$]*

O. N. Kazheva,[a]* G. G. Aleksandrov,[b] A. V. Kravchenko,[c] V. A. Starodub,[c,d] G. G. Zhigareva,[e] I. B. Sivaev,[e] V. I. Bregadze,[e] L. I. Buravov,[a] L. V. Titov,[a] and O. A. D′yachenko[a]

[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: koh@icp.ac.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279
[c]*V. N. Karazin Kharkov National University,*
4 pl. Svobody, 61077 Kharkov, Ukraine.
E-mail: twkravchenko@univer.kharkov.ua
[d]*Institute of Chemistry, Jan Kochanowski University, Kielce, Poland*
[e]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 6549. E-mail: sivaev@ineos.ac.ru

The radical cation salts of tetrathiafulvalene (TTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with iodo derivatives of cobalt bis(dicarbollide), (TTF)[9,9′,12,12′-I_4-3,3′-Co(1,2-$C_2B_9H_9$)$_2$] and (BEDT-TTF)[9,9′(12′)-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$], respectively, were synthesized and their crystal structures were determined. The introduction of iodine atoms into the lower rim of the dicarbollide ligands, unlike the substitution at the upper rim, leads to insignificant changes in the crystal structure and the conductivity of the radical cation salts compared to the analogous salts based on unsubstituted cobalt bis(dicarbollide).

Key words: cobalt bis(dicarbollide), tetrathiafulvalene, bis(ethylenedithio)tetrathiafulvalene, crystal structure, conductivity.

One of challenges of science and engineering is the design of new materials having combined properties. Molecular conductors traditionally occupy an important place among these materials. Nowadays, radical cation salts based on organic π-donors belong to the main class of molecular conductors. These compounds are of great interest because of the diversity of structural types and possibilities of varying the transport properties in a wide range. These quasi-two-dimensional systems have layered structures characterized by the presence of conducting radical cation layers alternating with anion layers. The cation and anion layers are spatially well separated in the crystal structures and form two sublattices. The conduction band is formed by the highest occupied molecular orbitals of radical cations. The anions that separate the radical cation layers have an effect on the packing mode of the donor molecules, which is responsible for the character of the transport properties. As a rule, the anions are not directly involved in the conduction process but, having specific properties (magnetic, photochromic, nonlinear optical, *etc.*), can be responsible for the corresponding physical properties of the crystals.[1,2]

The complementarity between organic and inorganic layers is of importance for the crystal formation of radical cation salts. The difference in the translation parameters of the sublattices can lead to the formation of both commensurate and incommensurate structural modulations. In the presence of the same donor, conductors having different structural and physical properties can be prepared by varying the composition of the anion sublattice.

The bis(dicarbollide) complexes of iron-subgroup metals [3,3′-M(1,2-$C_2B_9H_{11}$)$_2$]$^-$ (M = Fe, Co, and Ni) belong to a promising class of compounds for the design of molecular conductors due to their high stability, the possibility of varying the charge and the nature of the metal in

---

* Dedicated to Academician of the Russian Academy of Sciences I. L. Eremenko on the occasion of his 60th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1115—1121, June, 2010.

a wide range, and the modification of the starting bis(dicarbollide) by introducing various desired substituents.[3,4] Previously, we have investigated the influence of various substituents in the cobalt bis(dicarbollide) derivatives $[8,8'\text{-}X_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (X = H, Br, or I) on the crystal structures and the conductivities of molecular conductors based on radical cation salts of tetrathiafulvalene and its derivatives.[5—8] The aim of the present study was to synthesize and investigate radical cation salts with cobalt bis(dicarbollide) derivatives containing substituents in the lower rim of the dicarbollide ligand, *viz.*, $[9,9'(12')\text{-}I_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ and $[9,9',12,12'\text{-}I_4\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]^-$.

Results and Discussion

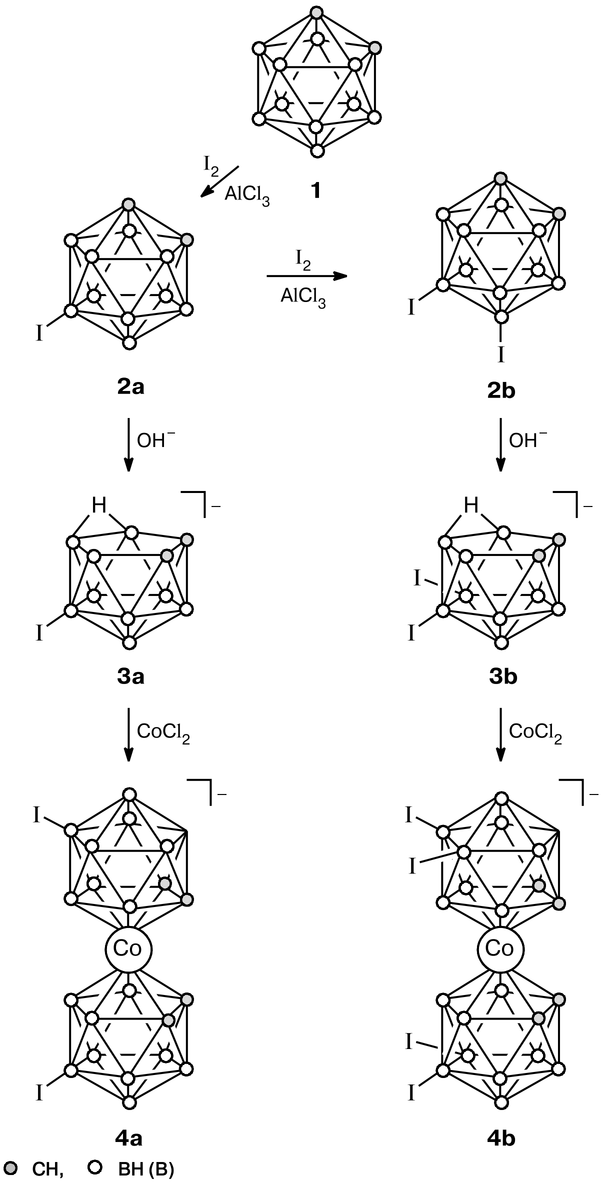
The investigation of tetrathiafulvaleniumyl (TTF) radical cation salts based on transition-metal bis(dicarbollide) complexes showed that the latter can play an active role in the formation of the crystal structures of molecular conductors depending on the mutual orientation of the dicarbollide ligands.[9] The asymmetry in the charge distribution in the dicarbollide anion can lead to a large difference in the dipole moments of different rotamers of bis(dicarbollide) (0, 5.4, and 3.1 D for the *anti*, *syn*, and *gauche* conformations, respectively).[10] At the same time, the differences between the energies of the conformers and the energy of the interconversions of the conformers are small (less than 11 and 41 kJ mol^{-1}, respectively).[11] Due to the low barriers to rotation, higher-energy rotamers can be stabilized in the solid state depending on the environment of the anion. Thus, the analysis of the data from the Cambridge Structural Database showed that the cobalt bis(dicarbollide) anion adopts the *anti* conformation in approximately 10% of the structures.[10] An increase in the energy of the barriers to rotation and the stabilization of particular conformers can be achieved by introducing different substituents into the carborane ligand.[12,13]

Previously, we have shown[8,9] that the replacement of hydrogen by halogen atoms at the boron atoms adjacent to the metal in positions 8 and 8′ of the dicarbollide ligand, as a rule, has only a slight effect on the crystal structure and the conductivity of cobalt bis(dicarbollide)-based tetrathiafulvaleniumyl salts. In addition to the size factor, the replacement leads to the stabilization of the *anti* rotamers of the metallacarborane anions having the smallest dipole moments through intramolecular B—X...H—C hydrogen bonds, as well as to the formation of intermolecular hydrogen bonds, which have the decisive effect on the formation of the anion sublattice.

In the present study, we investigated the radical cation salts of iodo derivatives of cobalt bis(dicarbollide)-containing substituents in the lower rim of the dicarbollide ligand (positions 9, 9′ and 12, 12′). It was expected that, unlike derivatives containing substituents in the upper rim of the dicarbollide ligand, whose *anti* conformation is to a great extent forced, the substitution at the lower rim would lead to a more free rotation of the dicarbollide ligands. This would be reflected in the crystal structure of molecular conductors based on these compounds.

Instead of the direct halogenation affording derivatives with substituents in positions 8 and 8′ of the dicarbollide ligand, another approach was applied to the synthesis of iodo derivatives containing substituents in the lower rim of the ligand. This was based on the iodination of *ortho*-carborane (1,2-dicarba-*closo*-dodecaborane (**1**)) followed by the transformation of the resulting iodo derivatives of *closo*-carborane **2a** and **2b** into the corresponding *nido*-carboranes **3a** and **3b** and their use in the synthesis of iodo derivatives of cobalt bis(dicarbollide) **4a** and **4b** (Scheme 1).

Scheme 1



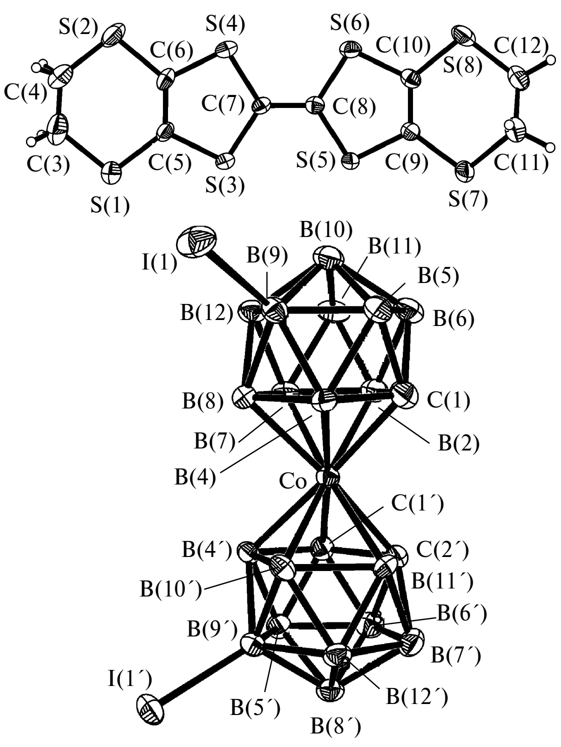


Fig. 1. Molecular structure of compound **5**.

Crystals of the radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and tetrathiafulvalene (TTF), *viz*., (BEDT-TTF)[9,9′(12′)-I_2-3,3′-Co-(1,2-$C_2B_9H_{10}$)$_2$] (**5**) and (TTF)[9,9′,12,12′-I_4-3,3′-Co-(1,2-$C_2B_9H_9$)$_2$] (**6**), respectively, were synthesized by the anodic oxidation of BEDT-TTF and TTF in 1,1,2-trichloroethane in the presence of 18-crown-6 and K[**4a**] or K[**4b**], respectively. The structures of the reaction products were established by X-ray diffraction.

The crystal structure of compound **5** consists of the radical cations BEDT-TTF and the anions [9,9′-I_2-3,3′-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$ occupying general positions (Fig. 1). The crystal packing of **5** can be arbitrarily referred to as a layered structure. Thus in spite of the alternation of the radical cation and anion layers along the *b* axis the radical cation layer is formed by the BEDT-TTF dimers, which are not linked together and do not form a conducting layer (Fig. 2). The interplanar distance between the dimers is 3.72 Å; the dihedral angle is 0° in accordance with the symmetry conditions; the short intermolecular S...S contacts in the dimers are 3.562(2) Å (S(3)...S(6)) (Fig. 3).

The radical cation BEDT-TTF$^{\bullet+}$ is nonplanar and adopts a chair conformation; the maximum deviation of the S(6) atom from the mean plane passing through the sulfur atoms is 0.14 Å; the deviations of the terminal car-

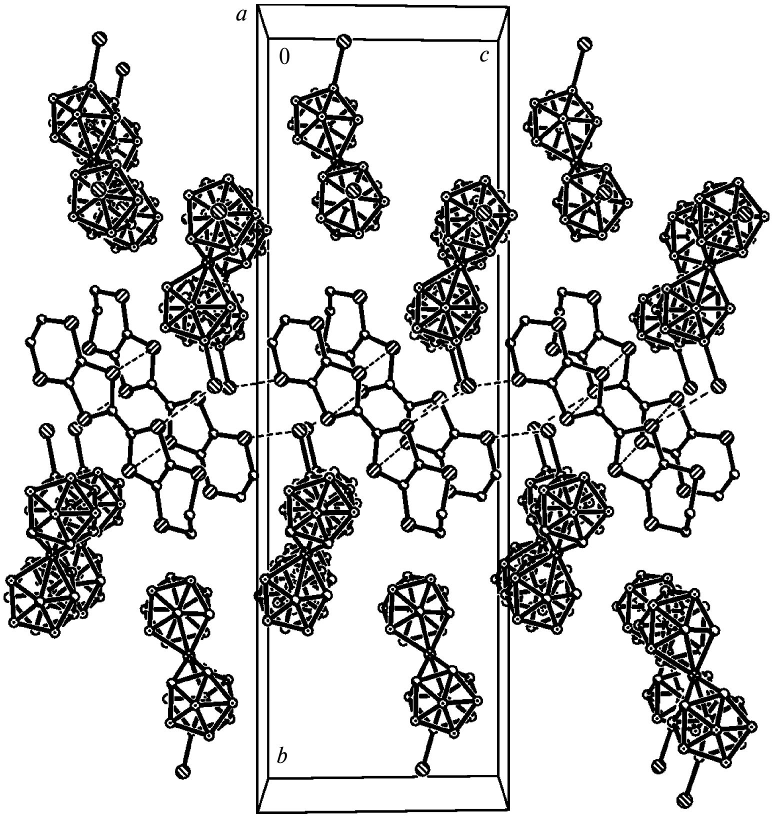


Fig. 2. Molecular packing in the crystal structure of **5**.

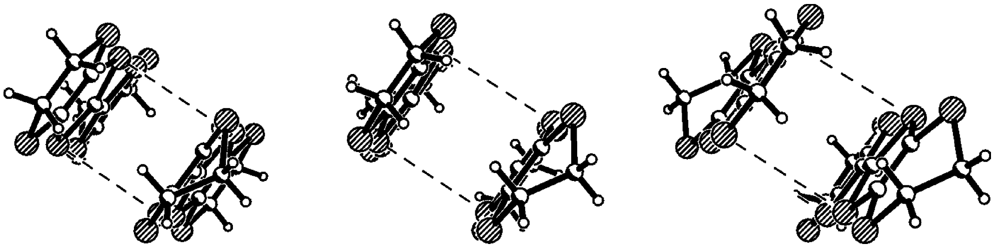


Fig. 3. Layer of the BEDT-TTF dimers in the crystal structure of compound **5**.

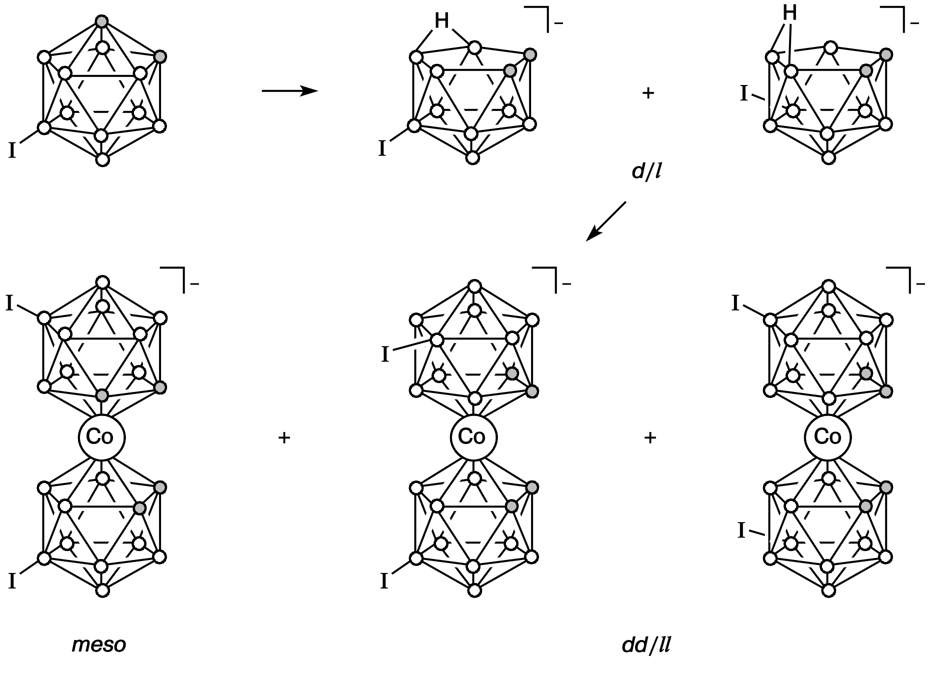
bon atoms C(11) and C(12) from this plane are +0.95 and –0.20 Å, respectively, The deviations of the disordered terminal atoms C(3) and C(4) are +0.49 and –0.23 Å, respectively (+0.14 and –0.61 Å for the C(3´) and C(4´) atoms, respectively).

Since the 9-iodo-*closo*-1,2-carborane molecule is prochiral, removal of one of the cage boron atoms results in the formation of an enantiomeric mixture of 5- and 6-iodo-7,8-dicarba-*nido*-undecaborates. In turn, the final cobalt bis(dicarbollide) exists as an inseparable mixture of the isomers *meso*-[9,9´-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$ and *rac*-[9(12),12´(9´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$ (Scheme 2).

As a result, the carbon atoms of the anion in the crystal structure of **5** are disordered (the Co—C and Co—B distances in the anion are 2.058(5)—2.072(5) Å and 2.087(5)—2.126(6) Å, respectively). The distance from the Co atom to the C_2B_3 plane is 1.48 Å, which is typical of the known salts and complexes with cobalt(III) bis(dicarbollide). The dicarbollide ligands in the anion [9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$ are twisted by 36° with respect to each other and adopt, like in the related salt with the unsubstituted anion [3,3´-Co(1,2-$C_2B_9H_{12})_2]^-$, the *syn* conformation, as opposed to the *anti* conformation characteristic of the salts with the anion [8,8´-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$. The dihedral angle between the C_2B_3 planes of the ligands is 2.9°. The B(9)—I(1) and B(9´)—I(1´) distances in the anion [9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$ are 2.189(6) and 2.178(5) Å, respectively, which are somewhat shorter than the B—I bonds in the anions [8-I-3,3´-Co(1,2-$C_2B_9H_{10}$)-(1´,2´-$C_2B_9H_{11})]^-$ (see Ref. 6) and [8,8´-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$ (see Ref. 8) (2.21—2.24 Å) and are similar to those in the iodo derivative of *ortho*-carborane 1,2-Ph_2-9-I-1,2-*closo*-$C_2B_{10}H_9$ (2.179 Å) with the similar arrangement of the substituent and the skeletal carbon atoms.[14]

In the structure of compound **5**, there are short intermolecular cation—anion contacts I(1)...S(2) (3.670(1) Å; the sums of the van der Waals radii are 3.60 Å (S...S) and 3.78 Å I...S)[15].

Scheme 2



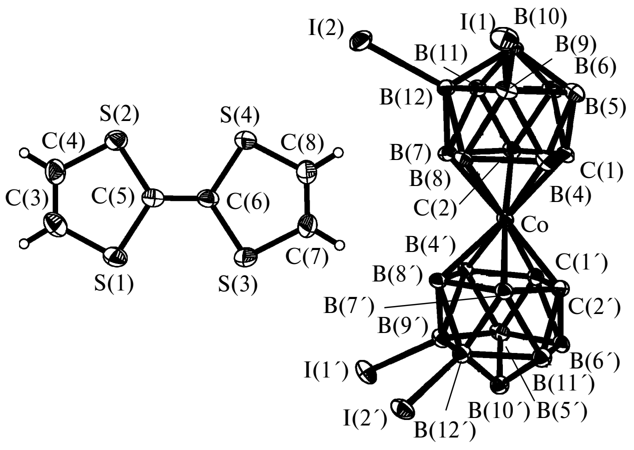


Fig. 4. Molecular structure of compound **6**.

The investigation of the conductivity of a single crystal of **5** showed that at room temperature this compound has semiconductor properties with $\sigma_{293} = 3 \cdot 10^{-5}$ Ohm^{-1} cm^{-1}, which is an order of magnitude smaller than the conductivity of the analogous salt with the unsubstituted anion (BEDT-TTF)$[3,3'$-Co$(1,2$-$C_2B_9H_{11})_2]$.[5] The temperature dependence of the resistance $\log[R(T)/R(293\text{ K})] = f(T^{-1})$ in the 220—293 K temperature range has an activation character with the activation energy $E_a \cong 0.29$ eV.

The crystal structure of (TTF)$[9,9',12,12'$-I_4-$3,3'$-Co$(1,2$-$C_2B_9H_9)_2]$ (**6**) consists of the radical cations TTF$^{\cdot+}$ and the anions $[9,9',12,12'$-I_4-$3,3'$-Co$(1,2$-$C_2B_9H_9)_2]^-$ occupying general positions (Fig. 4). The crystal packing of **6**, like that of **5**, can be arbitrarily referred to as a layered structure. In spite of the alternation of the radical cation and anion layers along the *b* axis, the radical cation layer is formed by stacks of the radical cations TTF$^{\bullet+}$ consisting of dimers, which are not linked together by short intermolecular contacts (Figs 5 and 6). The interplanar distance between the dimers is 3.48 Å; the dihedral angle is 0° in accordance with the symmetry conditions; the short intermolecular S...S contacts in the dimers are in the range of 3.423(2)—3.508(2) Å (the S(1)...S(4) and S(2)...S(3) contacts).

The radical cation TTF$^{\bullet+}$ adopts a virtually planar conformation; the maximum deviation of the atoms from the mean plane passing through all nonhydrogen atoms is 0.04 Å (the S(4) atom).

The Co—C and Co—B distances in the anion $[9,9'12,12'$-I_4-$3,3'$-Co$(1,2$-$C_2B_9H_9)_2]^-$ are 2.037(3)—2.049(4) Å and 2.069(4)—2.099(4) Å, respectively. The distance from the Co atom to the C_2B_3 plane is 1.46 Å, which is somewhat shorter than the corresponding distances in compounds **5** (1.48 Å) and (TTF)$[8,8'$-I_2-$3,3'$-Co$(1,2$-$C_2B_9H_{10})_2]$ (1.50 Å). The dicarbollide ligands are twisted with respect to each other by 36° and adopt the *syn* conformation. The dihedral angle between the C_2B_3 planes of the ligands is 4.0°. The B—I distances in the anion $[9,9'12,12'$-I_4-$3,3'$-Co$(1,2$-$C_2B_9H_9)_2]^-$ are in the range of 2.173(4)—2.185(4) Å and are similar to the corresponding distances in **5** and 9,12-diiodo-*ortho*-carborane **2b** (2.174 and 2.183 Å)[16] but

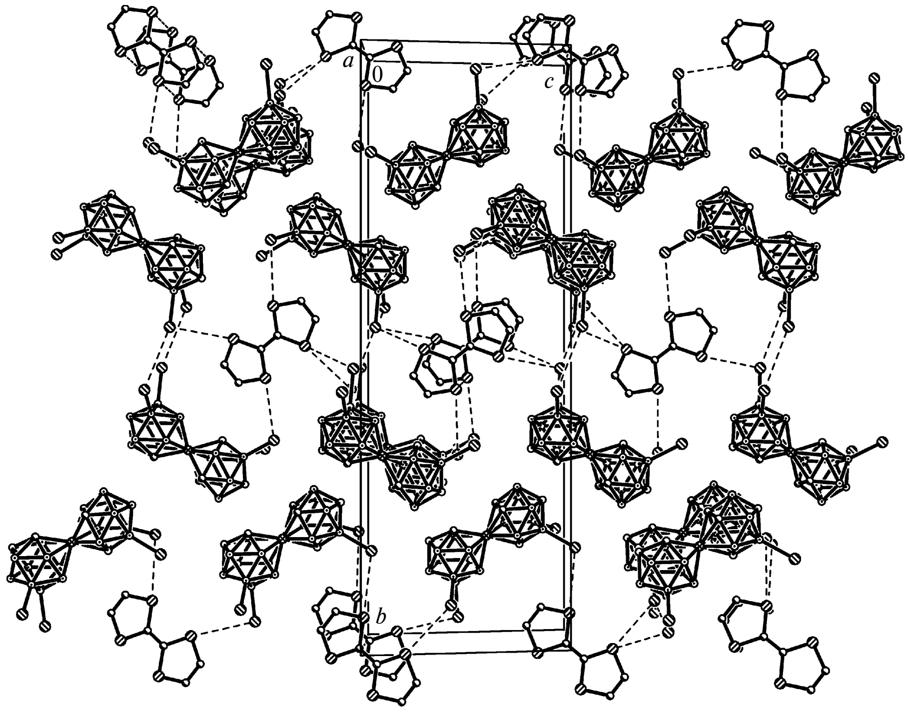


Fig. 5. Molecular packing in the crystal structure of **6**.

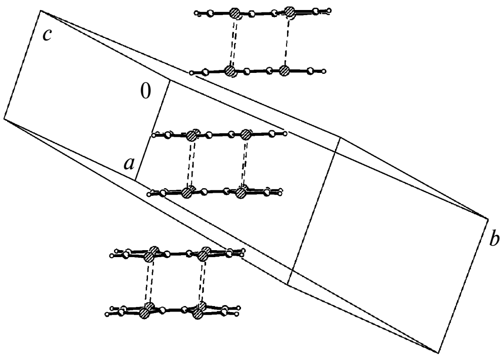


Fig. 6. TTF dimers in the crystal structure of compound **6**.

are shorter than that in the salt (TTF)[8,8´-I_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$] (2.216 Å).[8]

The anions are linked to each other by the short intermolecular I(1´)...I(2´) bonds (3.8587(5) Å, Fig. 7). There are also the following short intermolecular cation—anion contacts: I(1)...S(2), 3.802(1) Å; I(2)...S(3), 3.809(1) Å; I(1´)...S(1), 3.902(1) Å; I(2´)...S(1), 3.908(1) Å; I(2´)...S(4), 3.743(1) Å (the sums of the van der Waals radii are 3.60 Å (S...S), 3.96 Å (I...I), and 3.96 Å (I...S).[15]

The electrophysical measurements showed that at room temperature, salt **6** has semiconductor properties with $\sigma_{293} = 6 \cdot 10^{-7}$ Ohm^{-1} cm^{-1}, which is somewhat larger than that in the related salt with the unsubstituted anion (TTF)[3,3´-Co(1,2-$C_2B_9H_{11}$)$_2$][5] but is five orders of magnitude smaller than the conductivity of the salt (TTF)[8,8´-I_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$].[8] The temperature dependence $\log[R(T)/R(293\text{ K})] = f(T^{-1})$ in the 220—293 K temperature range has an activation character with the activation energy $E_a \cong 0.24$ eV.

Therefore, unlike derivatives containing iodine atoms in positions 8 and 8´ of the metallacarborane cage, the introduction of substituents in positions 9, 9´, 12 and 12´ leads only to slight changes in the crystal packing and the conductivity of the radical cation salts based on these compounds compared to the related salts of unsubstituted cobalt bis(dicarbollide). The differences between the derivatives containing iodine atoms in the upper and lower rims of the dicarbollide anion can be associated with the following three main factors: 1) the different conformations of the metallacarborane cage, and, as a consequence, their different dipole moments; 2) the different sizes of the anions; 3) the presence of intermolecular interactions through which the anions are linked together to form chains and layers. Presumably, the relatively small differences in the crystal structure and the conductivity of the radical cation salts based on unsubstituted cobalt bis(dicarbollide) and its 9,9´(12´)-diiodo and 9,9´,12,12´-tetraiodo derivatives are associated mainly with the size of the anion and, to a certain extent, with secondary intermolecular interactions. At the same time, differences in the structure and the conductivity of the radical cation salts containing substituents in different positions of the carborane ligand are associated primarily with the differences in the conformation and the dipole moment of the metallacarborane anions.

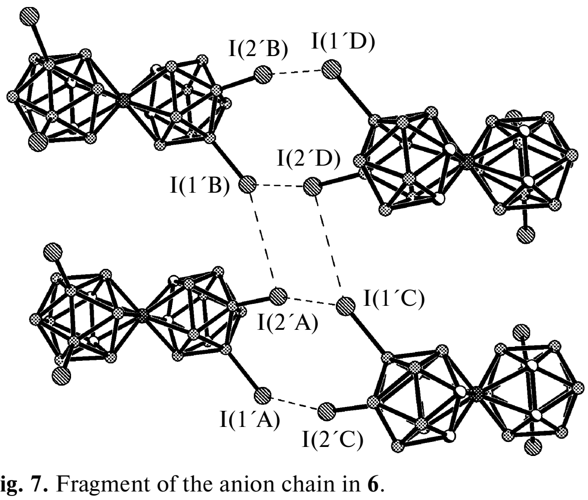


Fig. 7. Fragment of the anion chain in **6**.

To sum up, it can be concluded that the introduction of iodine atoms into the lower rim of the dicarbollide ligands, unlike the substitution at the upper rim, leads to insignificant changes in the crystal structure and the conductivity of the radical cation salts compared to the analogous salts based on cobalt bis(dicarbollide). Great differences in the structure and the conductivity of the radical cation salts containing substituents in different positions of the carborane ligand are apparently associated primarily with the differences in the conformation and the dipole moment of substituted metallacarborane anions.

Experimental

Tetrathiafulvalene (TTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Aldrich) were used without additional purification. 9,12-Diiodo-*ortho*-carborane (**2b**)[17] and K[9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$] (K[**4a**])[18] were synthesized as described in the literature. The ^{11}B NMR spectra were recorded on a Bruker Avance-400 spectrometer (operating at 128.38 MHz). The X-ray diffraction study of the salts (BEDT-TTF)[9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10}$)$_2$] (**5**) and (TTF)[9,9´,12,12´-I_4-3,3´-Co(1,2-$C_2B_9H_9$)$_2$] (**6**) was carried out on a Bruker SMART APEX2 CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique). The crystal structures were solved by direct methods followed by calculations of Fourier syntheses with the use of the SHELXS-97 program package.[19] The structures were refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms with the use of the SHELXL-97 program package.[20] The absorption correction was applied with the use of the APEX2 program.[21] The hydrogen atoms were positioned geometrically. The carbon atoms of one of the dicarbollide ligands in **5** are disordered over positions corresponding to the C(1) and B(7) atoms with occupancies of 0.56(4) and 0.44(4), respectively. The C(3) and C(4) atoms of the ethylene group of the BEDT-TTF

Table 1. Principal crystallographic data for (BEDT—TTF) [9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2$] (**5**) and (TTF)[9,9´,12,12´-I_4-3,3´-Co(1,2-$C_2B_9H_9)_2$] (**6**)

Compound	**5**	**6**
Formula	$C_{14}H_{28}B_{18}CoI_2S_8$	$C_{10}H_{22}B_{18}CoI_4S_4$
M	960.15	1031.63
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.2778(7)	7.7460(6)
b/Å	34.367(3)	33.876(3)
c/Å	10.7426(8)	11.808(1)
α/deg	90	90
β/deg	94.111(1)	98.933(1)
γ/deg	90	90
U/Å^3	3416.5(5)	3060.9(4)
Z	4	4
λ/Å	0.7107	0.7107
d_{calc}/g cm^{-3}	1.87	2.24
μ/mm^{-1}	2.813	4.875
Total number of reflections	28739	18555
Number of independent reflections	9513	9019
Number of reflections with [$F_0 > 4\sigma(F_0)$]	4759	5016
Number of refined parameters	408	334
$(2\theta)_{\max}$/deg	61.86	60.98
R	0.052	0.049

radical cation are disordered over two equally probable orientations with occupancies of 0.50(3). Principal crystallographic data for the compounds are given in Table 1. Bond lengths and bond angles are listed in Tables 2 and 3. The atomic coordinates, temperature factors, and geometric parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 728563 and 728562).

Table 2. Selected bond lengths (d) in compound **5**

Bond	d/Å	Bond	d/Å
Anion [9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2]^-$			
Co—C(1)	2.072(4)	Co—B(7)	2.087(5)
Co—C(1´)	2.058(4)	Co—B(8)	2.126(6)
Co—C(2)	2.062(4)	Co—B(10´)	2.114(4)
Co—C(2´)	2.069(5)	Co—B(11´)	2.099(5)
Co—B(4)	2.107(5)	I(1)—B(9)	2.189(5)
Co—B(4´)	2.089(4)	I(1´)—B(9´)	2.178(5)
Radical cation (BEDT—TTF)$^{\bullet+}$			
C(7)—C(8)	1.383(6)	S(4)—C(6)	1.729(5)
S(3)—C(7)	1.725(5)	S(5)—C(9)	1.743(5)
S(4)—C(7)	1.722(4)	S(6)—C(10)	1.729(5)
S(5)—C(8)	1.736(4)	C(5)—C(6)	1.360(7)
S(6)—C(8)	1.720(5)	C(9)—C(10)	1.369(6)
S(3)—C(5)	1.737(4)		

Table 3. Selected bond lengths (d) in compound **6**

Bond	d/Å	Bond	d/Å
Anion [9,9´,12,12´-I_4-3,3´-Co(1,2-$C_2B_9H_9)_2]^-$			
Co—C(1)	2.041(4)	Co—B(7´)	2.077(4)
Co—C(1´)	2.049(4)	Co—B(8)	2.099(4)
Co—C(2)	2.041(4)	Co—B(8´)	2.097(4)
Co—C(2´)	2.037(3)	I(1)—B(9)	2.185(4)
Co—B(4)	2.097(4)	I(1´)—B(9´)	2.173(4)
Co—B(4´)	2.087(4)	I(2)—B(12)	2.175(4)
Co—B(7)	2.069(4)	I(2´)—B(12´)	2.176(4)
Radical cation (TTF)$^{\bullet+}$			
C(5)—C(6)	1.368(6)	S(2)—C(4)	1.720(5)
S(1)—C(5)	1.738(4)	S(3)—C(7)	1.721(5)
S(2)—C(5)	1.715(5)	S(4)—C(8)	1.712(5)
S(3)—C(6)	1.731(5)	C(3)—C(4)	1.322(7)
S(4)—C(6)	1.724(4)	C(7)—C(8)	1.334(7)
S(1)—C(3)	1.707(6)		

The conducting properties of the crystals were studied on an automated device for measurements of the temperature dependence of the resistance by the four-probe method in the range of 220—295 K at a direct current. The rate of the change of the temperature the samples was ~1 K min^{-1}.

Trimethylammonium 5,6-diiododecahydro-7,8-dicarba-*nido*-undecaborate ((Me$_3$NH)[3b]). Potassium hydroxide (1.71 g, 30 mmol) was added to a solution of **2b** (3.98 g, 10 mmol) in ethanol (150 mL), and the reaction mixture was refluxed for 8 h. Then the solution was cooled, decanted, and concentrated. The residue was dissolved in water (100 mL), filtered, and treated with an aqueous solution of trimethylammonium chloride (1.45 g, 15 mmol). The precipitate that formed was filtered off and dried in air. A white product was obtained in a yield of 3.89 g (87%). Found (%): C, 12.93; H, 4.37; B, 21.63. $C_5H_{20}B_9CI_2N$. Calculated (%): C, 13.47; H, 4.52; B, 21.86. ^{11}B NMR (acetone-d$_6$), δ: −9.4 (d, 2 B); −17.0 (d, 1 B); −21.1 (d, 2 B); −24.1 (s, 2 B); −27.8 (d, 1 B); −33.6 (d, 1 B).

Potassium 9,9´(12´)-diiodoicosahydro-1,1´,2,2´-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (K[4b]). The compound (Me$_3$NH)[**3b**] (4.59 g, 10 mmol) and $CoCl_2 \cdot 6H_2O$ (3.56 g, 15 mmol) were added to 40% aqueous KOH. The reaction mixture was refluxed for 12 h, cooled, diluted with water to 200 mL, and extracted with Et$_2$O (3 x 200 mL). The organic layer was dried with Na$_2$SO$_4$ and concentrated to dryness. After chromatographic purification (silica gel, acetone—dichloromethane, 1 : 5), a brick-red product was obtained in a yield of 4.35 g (50%). Found (%): C, 5.23; H, 1.97; B, 22.64. $C_4H_{18}B_{18}CoI_4K$. Calculated (%): C, 5.55; H, 2.09; B, 22.46. ^{11}B NMR (acetone-d$_6$), δ: −7.0 (d, 2 B); −4.8 (d, 2 B); −5.6 (d, 4 B); −15.6 (s, 4 B + d, 4 B); −22.2 (d, 2 B).

Bis(ethylenedithio)tetrathiafulvaleniumyl 9,9´(12´)-diiodo-icosahydro-1,1´,2,2´-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (5) and tetrathiafulvaleniumyl 9,9´,12,12´-tetraiodooctadecahydro-1,1´,2,2´-tetracarba-3-*commo*-cobalta-*closo*-tricosaborate (6). The radical cation salts (BEDT-TTF)[9,9´(12´)-I_2-3,3´-Co(1,2-$C_2B_9H_{10})_2$] (**5**) and (TTF)[9,9´,12,12´-I_4-3,3´-Co(1,2-$C_2B_9H_9)_2$] (**6**) were obtained as black sparkling needle-like crystals by the anodic oxidation of BEDT-TTF and

TTF, respectively, in 1,1,2-trichloroethane in the presence of 18-crown-6 and K[**4a**] or K[**4b**], respectively. Crystals of **5** and **6** were grown by the electrochemical crystallization in a galvanostatic mode in a two-electrode cell with a glass membrane at platinum electrodes. The current was increased stepwise each day by 0.05 μA from 0.1 to 1.2—1.5 μA. The period of the crystal growth was 4—5 weeks. Crystals of **5** were obtained in the $K[9,9'(12')-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ ($1 \cdot 10^{-2}$ mol L^{-1}) — 18-crown-6 ($2.5 \cdot 10^{-2}$ mol L^{-1}) — BEDT-TTF ($2 \cdot 10^{-3}$ mol L^{-1}) — 1,1,2-trichloroethane system. Crystals of **6** were obtained in the $K[9,9',12,12'-I_4-3,3'-Co(1,2-C_2B_9H_9)_2]$ ($8 \cdot 10^{-3}$ mol L^{-1}) — 18-crown-6 ($2 \cdot 10^{-2}$ mol L^{-1}) — TTF ($2 \cdot 10^{-3}$ mol L^{-1}) — 1,1,2-trichloroethane system.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 07-03-00712 and 08-03-12043).

References

1. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. H. Whangbo, *Organic Superconductors (Including Fullerenes: Synthesis, Structure, Properties, and Theory)*, Prentice Hall, Englewood Cliffs, New Jersey, 1992.
2. T. Ishiguro, K. Yamaji, G. Saito, *Organic Superconductors*, 2nd ed., Springer Ser. Solid-State Sci., Springer, Berlin, 1998.
3. I. B. Sivaev, V. I. Bregadze, *Collect. Czech. Chem. Commun.*, 1999, **64**, 783.
4. V. I. Bregadze, S. V. Timofeev, I. B. Sivaev, I. A. Lobanova, *Usp. Khim.*, 2004, **73**, 470 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2004, **73**, 433].
5. O. N. Kazheva, A. N. Chekhlov, G. G. Alexandrov, L. I. Buravov, A. V. Kravchenko, V. A. Starodub, I. B. Sivaev, V. I. Bregadze, O. A. Dyachenko, *J. Organomet. Chem.*, 2006, **691**, 4225.
6. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, V. A. Starodub, I. B. Sivaev, I. A. Lobanova, V. I. Bregadze, L. I. Buravov, O. A. Dyachenko, *J. Organomet. Chem.*, 2007, **692**, 5033.
7. O. Kazheva, G. Alexandrov, A. Kravchenko, V. Starodub, I. Lobanova, I. Sivaev, V. Bregadze, L. Buravov, O. Dyachenko, *Solid State Sci.*, 2008, **10**, 1734.
8. O. N. Kazheva, G. G. Alexandrov, A. V. Kravchenko, V. A. Starodub, I. A. Lobanova, I. B. Sivaev, V. I. Bregadze, L. V. Titov, L. I. Buravov, O. A. Dyachenko, *J. Organomet. Chem.*, 2009, **694**, 2336.
9. V. Bregadze, I. Sivaev, I. Lobanova, A. Kravchenko, V. Starodub, O. Kazheva, G. Alexandrov, L. Titov, L. Buravov, O. Dyachenko, *J. Chem. Sci.*, 2010, **122**, 37.
10. E. J. Juarez-Perez, PhD Thesis, Barcelona, 2009.
11. M. Bühl, D. Hnyk, J. Machaček, *Chem. Eur. J.*, 2005, **11**, 4109.
12. R. Nuñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, *Chem. Eur. J.*, 2005, **11**, 5637.
13. R. D. Kennedy, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, 2009, **48**, 9377.
14. T. D. McGrath, M. A. Fox, A. J. Welch, *Acta Cryst.*, 2000, **C56**, 487.
15. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
16. A. S. Batsanov, M. A. Fox, J. A. K. Howard, A. K. Hughes, A. L. Johnson, S. J. Martindale, *Acta Crystallogr. Sect. C*, 2003, **59**, o74.
17. L. I. Zakharkin, V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 575 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1966, **15**, 549].
18. L. I. Zakharkin, V. A. Ol´shevskaya, E. V. Balagurova, P. V. Petrovskii, *Zh. Obshch. Khim.*, 2000, **70**, 590 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2000, **70**, 550].
19. G. M. Sheldrick, SHELXS 97, University of Göttingen, Göttingen, Germany, 1997.
20. G. M. Sheldrick, SHELXL 97, University of Göttingen, Göttingen, Germany, 1997.
21. APEX2 Softwarwe Package, Bruker AXS, Madison, Wisconsin, USA, 2005.

Received August 19, 2009;
in revised form March 18, 2010