



## Molecular conductors with 8,8'-diiodo cobalt bis(dicarbollide) anion

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### ABSTRACT

New molecular conductors on the base of 8,8'-diiodo cobalt bis(dicarbollide) anion (TTF)[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (**1**), (BMDT-TTF)<sub>4</sub>[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (**2**) and (BEDT-TTF)<sub>2</sub>[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (**3**) were synthesized and their crystal structures and electrical conductivities were determined. All the radical cation salts prepared were found to be semiconductors. Some regularities in the crystal structures of the TTF-based radical cation salts with bis(dicarbollide) complexes of transition metals are discussed.

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## 1. Introduction

Radical cation salts and charge-transfer complexes based on tetrathiafulvalene (TTF) and their derivatives constitute a wide class of organic materials with transport properties ranging from insulating to superconducting [1,2]. Conductivity in these materials occurs *via* the  $\pi$ -electron donor network made up of stacks or sheets of closely packed radical cations. The packing of radical cations in the solid state was found to be a crucial parameter determining conductivity of the target compound. At the same time, the oxidation potentials of the TTF ring system can be finely tuned by attachment of electron-donating or electron-withdrawing substituents. It caused incredible interest in syntheses of TTF-based molecules [3,4].

On the other hand, the radical cation packing in molecular materials depends strongly on the nature of counterions. Until relatively recently the main interest in this class of compounds was focused on their transport properties. A hot focus of research in contemporary material science is building multifunctionality of materials and current synthetic efforts are aimed towards to design novel materials that combine in the same crystal lattice

two or more physical properties which are difficult or impossible to achieve in continuous lattice solids. Since the majority of the TTF-based salts consist of discrete layers of cationic and anionic components, it should be possible to prepare new molecular materials with coexistence of properties, or materials exhibiting novel properties due to the mutual interaction between the different layers or individual networks. As a result, increasing attention is now being focused on synthesis of magnetic molecular conductors, where components with magnetic properties can be introduced by anionic complexes with paramagnetic centers [5,6]. Organometallic chemistry provides a wide choice of metal complexes of various sizes and charges that can be used as charge-compensating counterions of the conducting radical cation salts. The bis(1,2-dicarbollide) complexes of the iron group metals, [*commo*-3,3'-M(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> (M = Fe, Co, Ni), are known to demonstrate extraordinary high stability due to delocalized cluster bonding of the metal atom with  $\pi$  orbitals of the dicarbollide ligands [7,8] and can be considered as charge-compensating counterions for synthesis of new radical cation-based molecular materials [9]. The hydrogen atoms in these compounds can be easily substituted for various atoms and groups, which open practically unlimited perspectives of their modification. By this way, counter ions of increasing complexity, with a variety of volumes, connectivity, shapes and charges can be prepared [7,8,10].

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Moreover, an introduction of substituents which are capable of hydrogen bond formation provides important strategy for molecular design to control molecular arrangement in charge-transfer complexes and salts [11].

Recently we started study of effect of different substituents in the iron group metal bis(1,2-dicarbollide) complexes on crystal packing and physical properties of their salts with TTF-based radical cations [12–14]. In this report we describe synthesis, crystal structure and electrical conductivity of tetrathiafulvalenium salts of 8,8'-diiodo derivative of cobalt bis(dicarbollide) anion  $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ .

## 2. Experimental

### 2.1. Synthesis

Tetrathiafulvalene (TTF), bis(methylenedithio)tetrathiafulvalene (BMDT-TTF), and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Aldrich) were used as received.  $K[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  was prepared as previously described [15]. New radical cation salts (TTF) $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**1**), (BMDT-TTF) $_4[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**2**) and (BEDT-TTF) $_2[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**3**) were grown by anodic oxidation of tetrathiafulvalene, bis(methylenedithio)-tetrathiafulvalene and bis(ethylenedithio)-tetrathiafulvalene, respectively, in the presence of  $K[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  and 18-crown-6 under argon atmosphere. The crystals were grown by electrochemical crystallization under galvanostatic conditions in standard two-electrode H-cell with platinum electrodes separated by glass frit. The current applied was changed discretely on 0.05–0.10 mA per day from 0.10 to 1.00 mA. The period of crystal growth was 3–5 weeks.

Crystals of **1** were obtained from the  $K[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  ( $8 \times 10^{-3}$  M) – 18-crown-6 ( $1.5 \times 10^{-2}$  M) – TTF ( $2 \times 10^{-3}$  M) system using 1,1,2-trichloroethane as a solvent. Crystals of **2** were obtained from the  $K[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  ( $8 \times 10^{-3}$  M) – 18-crown-6 ( $1.5 \times 10^{-2}$  M) – BMDT-TTF ( $2 \times 10^{-3}$  M) system using 1,1,2-trichloroethane or 1,1,2-trichloroethane–acetonitrile (20:1) as solvents. Crystals of **3** were obtained from the  $K[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  ( $8 \times 10^{-3}$  M) – 18-crown-6 ( $1.5 \times 10^{-2}$  M) – BEDT-TTF ( $2 \times 10^{-3}$  M) system using 1,1,2-trichloroethane as a solvent.

### 2.2. Single-crystal structure determination

X-ray diffraction studies of (TTF) $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**1**) and (BEDT-TTF) $_2[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**3**) were carried out with a Bruker-P4 diffractometer, using graphite monochromated Mo K $\alpha$  radiation ( $\omega$ -scanning), whereas X-ray diffraction study of (BMDT-TTF) $_4[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**2**) was carried out with a Enraf-Nonius CAD-4 diffractometer, using graphite monochromated Cu K $\alpha$  radiation ( $\omega$ -scanning). The structures were solved by direct methods followed by Fourier difference syntheses using SHELXS software [16] and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms using SHELXL software [17]. The reflection intensities were corrected for absorption using semi-empirical method [18]. The hydrogen atoms were located from the geometry conditions. The relatively high final *R* factor of 9.8% for **3** was due to the poor quality of crystals. Nevertheless, the composition and the crystal molecular structure of **3** are unambiguous.

Details concerning the crystal data collection and refinement parameters for compounds **1–3** are summarized in Table 1. Selected bond lengths are listed in Tables S1–S3.

### 2.3. Electric resistivity measurements

The temperature dependence of electric resistivity was measured on single crystal samples of **1** and **2** and polycrystalline sample of **3**, using standard dc-four-probe technique. The crystals preliminary were glued on the module with four platinum thin wire of diameter 15  $\mu$ m with the aid of conducting graphite paint. The module was mounted inside of stainless-steel light-wall tube (diameter  $\sim$ 11 mm), and the tube was slowly inserted to the transport helium jar with gradual cooling of the sample from 293 K to 72 K with cooling rate of 50–60 K/h.

## 3. Results and discussions

The bis(1,2-dicarbollide) complexes of the iron group metals  $[3,3'-M(1,2-C_2B_9H_{10})_2]^-$  (*M* = Fe, Co, Ni) [7,8] are known to demonstrate extraordinary stability due to the delocalized cluster bonding the transition metal with ligand orbitals and can be considered as charge-compensating counterions for synthesis of new radical cation-based molecular materials [12,19–21]. These

**Table 1**

Crystal data and structure refinement for (TTF) $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**1**), (BMDT-TTF) $_4[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**2**), (BEDT-TTF) $_2[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$  (**3**).

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empiric formula	C <sub>10</sub> H <sub>24</sub> B <sub>18</sub> CoI <sub>2</sub> S <sub>4</sub>	C <sub>36</sub> H <sub>36</sub> B <sub>18</sub> CoI <sub>2</sub> S <sub>32</sub>	C <sub>24</sub> H <sub>36</sub> B <sub>18</sub> CoI <sub>2</sub> S <sub>16</sub>
Formula weight	779.84	2001.88	1344.80
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	7.2212(8)	10.954(1)	6.981(1)
<i>b</i> (Å)	9.717(1)	16.426(1)	8.984(1)
<i>c</i> (Å)	11.624(1)	20.146(1)	21.325(1)
$\alpha$ (°)	108.407(7)	98.64(1)	97.17(1)
$\beta$ (°)	99.341(6)	95.68(1)	91.35(1)
$\gamma$ (°)	107.403(6)	107.77(1)	112.50(1)
<i>V</i> (Å <sup>3</sup> )	708.2(1)	3372.1(4)	1222.3(2)
<i>Z</i>	1	2	1
$\lambda$ (Å)	0.71073	1.5418	0.71073
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.83	1.97	1.83
$\mu$ (mm <sup>-1</sup> )	3.085	18.733	2.324
Number of reflections collected	4421	11960	6537
Number of independent reflections	3979	11960	5284
Number of reflections with $[F_0 > 4\sigma(F_0)]$	3288	8849	3408
Number of parameters refined	161	806	277
( $2\theta$ ) <sub>max</sub> (°)	60.00	149.82	55.08
<i>R</i>	0.040	0.068	0.098

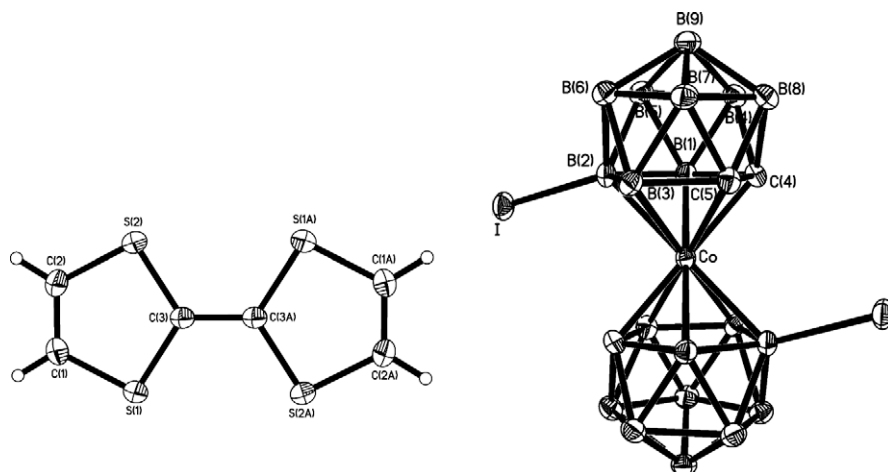


Fig. 1. Atom designations in (TTF)[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1).

complexes could be easily modified by substitution of hydrogen atoms at carbon and boron atoms of the dicarbollide ligands for various non-hydrogen atoms and functional groups [7,8,10]. The bis(1,2-dicarbollide) complexes have very close dimensions and demonstrate rather similar chemical properties, whereas their magnetic characteristics are different. It should be noted that diamagnetic cobalt bis(dicarbollide) and their derivatives at present are much more studied than their paramagnetic iron and nickel analogues. The main reason here is simple and reliable characterization of diamagnetic compounds by methods of NMR spectroscopy, whereas characterization of substituted paramagnetic compounds, especially substituted derivatives, are rather difficult and tedious. However, very close shape and size of the bis(dicarbollide) complexes give possibility to use diamagnetic cobalt bis(dicarbollide)s as model compounds for crystal structure design of molecular materials containing related paramagnetic counterions.

Some limitations of this model are connected with mutual rotation of the dicarbollide ligands. It was shown that *cisoid* and *transoid* conformations are preferable for cobalt(III) and nickel(III) bis(1,2-dicarbollide), respectively [7,8]. The asymmetry of charge distribution in the dicarbollide ligand (positive charge on the CH hydrogen atoms and the most negative charge on the opposite side of the ligand) results in rather high dipole moment of bis(dicarbollide) anion in *cisoid* conformation and an absence or very low dipole moment in *transoid* conformation. It could result in different crystal packing bis(dicarbollide) anions in *transoid* and *cisoid* conformations and this possibility cannot be ruled out in the case of unsubstituted bis(dicarbollide) complexes.

In general, calculated energy difference between the rotational conformers in the case of unsubstituted dicarbollide ligands is rather low (approx. 10–12 kJ/mol) [22,23] and the corresponding interconversion barriers are low as well. As a result, easy rotation of the dicarbollide ligands could produce different conformations under action of small external factors such as crystal packing. The characteristic example is coexistence of different conformations (*cisoid* and *transoid*) of the cobalt bis(dicarbollide) anion in the structure of [Mn(Phen)<sub>3</sub>][3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sub>2</sub> [24]. The difference in the rotational conformer energy could be enlarged by substitution of hydrogen atoms in the dicarbollide ligand for different atoms and groups resulting in stabilization of a single conformer, as a rule *transoid* one. On the other hand, an introduction of various substituents in the dicarbollide ligand gives possibility to vary size and shape of the bis(dicarbollide) anions that is an important precondition of effective crystal design of molecular

materials. As a result, substituted cobalt bis(dicarbollide)s could serve as model compounds for crystal engineering and fine tuning of electric and magnetic properties of molecular materials.

Recently we started study of effect of different substituents in the iron group metal bis(1,2-dicarbollide) complexes on crystal packing and physical properties of their salts with TTF-based radical cations and reported a series of TTF-based salts with unsubstituted, monoiodo- and dibromo-substituted bis(dicarbollide) complexes [12–14]. In this report we describe synthesis, crystal structure and electrical conductivity of tetrathiafulvalenium salts of 8,8'-diiodo derivative of cobalt bis(dicarbollide) anion [8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup>.

(TTF)[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1), (BMDT-TTF)<sub>4</sub>[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (2) and (BEDT-TTF)<sub>2</sub>[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (3) crystals were prepared by electrochemical anodic oxidation of the corresponding  $\pi$ -donors in the presence of K[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] and 18-crown-6 as an additional component to increase solubility of the cobaltacarborane salt.

The crystal structure of 1 is formed by the TTF radical cations and the [8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> anions in special centrosymmetric positions (Fig. 1). The anions form lines along the *a* and *c*-axes, whereas single TTF radical cations are located in the between of the anion lines (Fig. 2). The TTF radical cations are planar

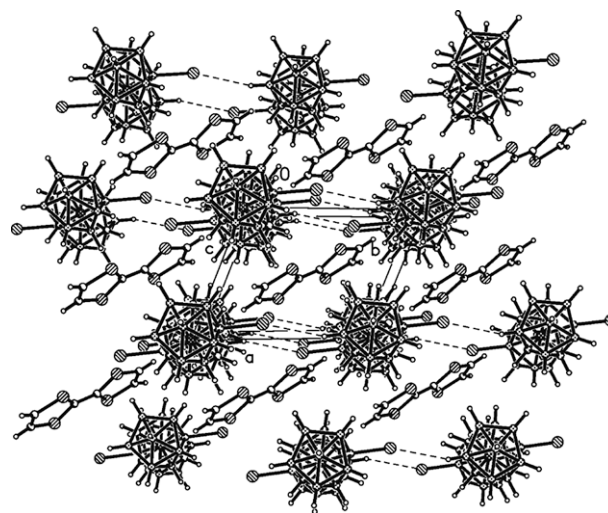


Fig. 2. A fragment of crystal structure of (TTF)[8,8'-I<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (1).

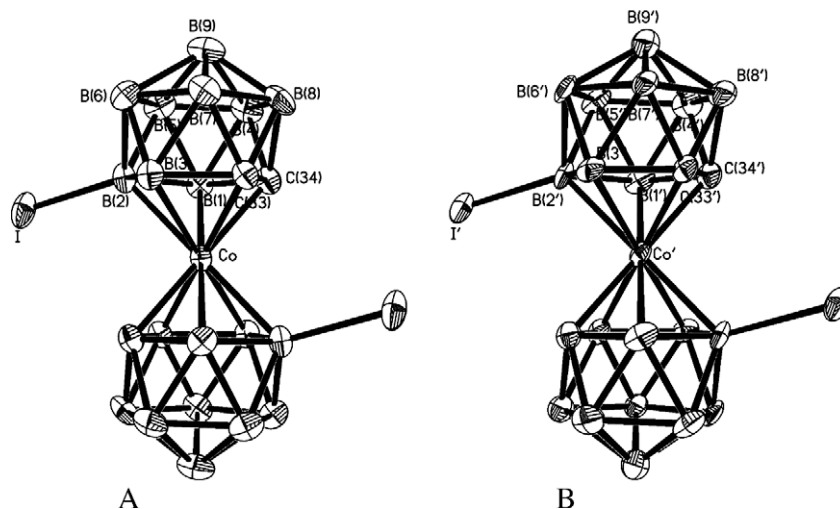


Fig. 3. Atom designations in  $(\text{BMDT-TTF})_4[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**).

according to the symmetry conditions. Using the empirical correlation between C=C and C–S bond lengths and the charges for TTF salts [25,26], the charge of tetrathiafulvalenium radical cation in

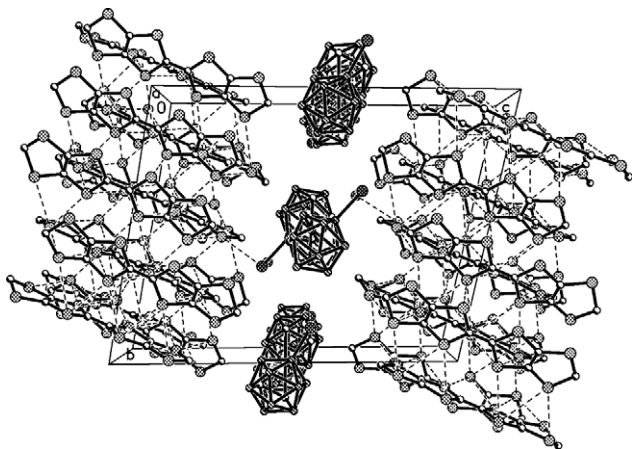


Fig. 4. A fragment of crystal structure of  $(\text{BMDT-TTF})_4[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**).

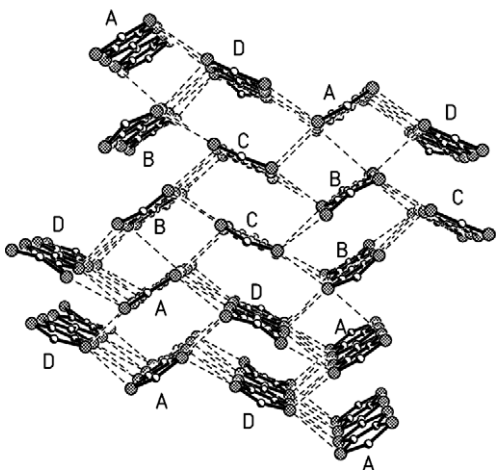


Fig. 5. Packing the BMDT-TTF cation radicals in  $(\text{BMDT-TTF})_4[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**).

**1** was found to be +1 that agrees well with the compound stoichiometry.

The geometry of the  $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  anion in **1** is close to that found in  $\text{Cs}[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  [27]. The dicarbollide ligands are mutually rotated by  $180^\circ$  producing transoid conformation. The  $\text{C}_2\text{B}_3$  faces are parallel on symmetry conditions. The distances from the cobalt atom to the  $\text{C}_2\text{B}_3$  planes are equal 1.50 Å, the average Co–C and Co–B bonds are 2.045 and 2.149 Å, respectively. The B–I distance is 2.216(3) Å.

$(\text{BMDT-TTF})_4[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**) was found to be isostructural with the corresponding bromo derivative  $(\text{BMDT-TTF})_4[8,8'\text{-Br}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  described earlier [14]. The asymmetric cell unit of **2** contains four crystallographically independent BMDT-TTF radical cations, labelled A, B, C and D, in general positions and two independent halves of  $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  anions (A and B) in the special centrosymmetric positions (Fig. 3). In common with many BEDT-TTF charge-transfer salts, the crystal packing consists of cationic and anionic layers alternating along the *c*-axis (Fig. 4). The structure of the organic layer is reminiscent of the well known  $\alpha$ -type in the BEDT-TTF series. In the BMDT-TTF layer, there are two types of different stacks, the first one is formed by the A and B donor molecules alternating in the –A–A–B–B– order and second one is formed by the C and D molecules in the –C–C–D–D– alternate arrangement (Fig. 5). The radical cations are nearly planar, the maximum deviation of sulfur atoms from the cation plane being 0.18 Å and deviations of terminal carbon atoms amounting 0.33 Å. Dihedral angles formed by the BMDT-TTF molecules from different stacks were found to be A–C  $56.4^\circ$ , A–D  $57.1^\circ$ , B–C  $57.7^\circ$ , and B–D  $58.4^\circ$ . The donor molecules of different types in stacks (A–B and C–D) are near parallel (dihedral

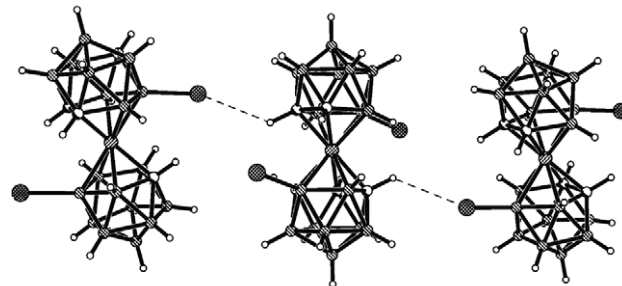


Fig. 6. Anion chains in  $(\text{BMDT-TTF})_4[3,3'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**).

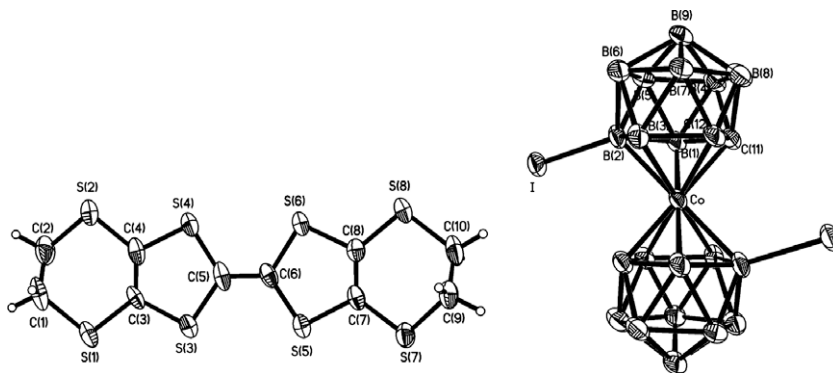


Fig. 7. Atom designations in  $(\text{BEDT-TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**3**).

dral angles are  $1.4\text{--}2.2^\circ$ ), whereas donors of the same type (A–A, B–B, C–C and D–D) are parallel on the symmetry conditions. The stacks are noticeably dimerized, the distances between the donor planes are  $3.58\text{ \AA}$  for A–A,  $3.50\text{ \AA}$  for B–B,  $3.68\text{ \AA}$  for A–B,  $3.56\text{ \AA}$  for C–C,  $3.52\text{ \AA}$  for D–D, and  $3.69\text{ \AA}$  for C–D. There are many shortened  $\text{S}\cdots\text{S}$  contacts of side-to-side mode between adjacent BMDT-TTF cation stacks (interstack contacts) ranging from  $3.369(2)$  to  $3.626(2)\text{ \AA}$  (sum of van der Waals radii is  $3.68\text{ \AA}$  [28]) (Table S4).

The geometry of the  $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  anion in **2** is similar to those found in **1** and  $\text{Cs}[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$ . The dicarbollide ligands have transoid conformation. The  $\text{C}_2\text{B}_3$  faces are parallel on symmetry conditions. The distances from the cobalt atom to the  $\text{C}_2\text{B}_3$  planes for the A and B anions are equal  $1.50$  and  $1.48\text{ \AA}$ , respectively. The average Co–C and Co–B bonds are  $2.025$  and  $2.130\text{ \AA}$ . The B–I distances are  $2.175(8)$  and

$2.206(6)\text{ \AA}$  for the A and B anions, respectively. The transoid conformation is stabilized by formation of intramolecular hydrogen  $\text{CH}\cdots\text{IB}$  bonds ( $2.94\text{--}3.00\text{ \AA}$ , sum of van der Waals radii is  $3.14\text{ \AA}$  [28]) between the dicarbollide ligands.

In the anion layer, the  $\text{CH}\cdots\text{IB}$  hydrogen intermolecular bonds of  $2.99\text{ \AA}$  connect the cobaltacarborane anions into infinite length chains (Fig. 6). Additional  $\text{S}(17)\cdots\text{I}$  contacts of  $3.747(2)\text{ \AA}$  (sum of van der Waals radii is  $3.98\text{ \AA}$  [28]) were found between the cation and anion layers (see Figs. 7–9).

$(\text{BEDT-TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**3**) was found to be isostructural with the earlier described monoiodo and dibromo derivatives,  $(\text{BEDT-TTF})_2[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$  [13] and  $(\text{BMDT-TTF})_4[8,8'\text{-Br}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  [14] described earlier. Crystal structure of **3** is formed by BEDT-TTF radical cations in general positions and  $[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  anion in the special centrosymmetric position. The crystal packing consists of cationic and anionic layers alternating along the  $c$ -axis. The arrangement of donor molecules in conducting layer resembles  $\beta$ -type packing motif. The BEDT-TTF stacks are irregular and contain dimer pairs. The interplanar distances in the pairs were found to be  $3.64\text{ \AA}$ , whereas distances between pairs are  $3.84\text{ \AA}$ . The  $\text{S}\cdots\text{S}$  contacts  $3.586\text{ \AA}$  were found between adjacent stacks of the BEDT-TTF donors. Dihedral angles formed by the donor molecules are  $0^\circ$ . The  $\text{S}\cdots\text{S}$  contacts  $3.586\text{ \AA}$  were found between adjacent stacks of the BEDT-TTF donors. The BEDT-TTF radical cations are not planar, the maximum deviation of sulfur atoms from the donor plane being  $0.18\text{ \AA}$  and deviations of the carbon atoms of

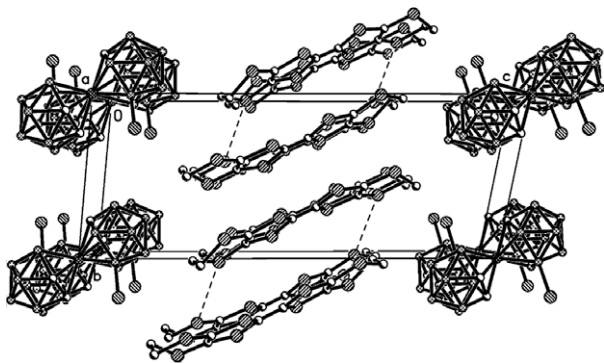


Fig. 8. A fragment of crystal structure of  $(\text{BEDT-TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**3**).

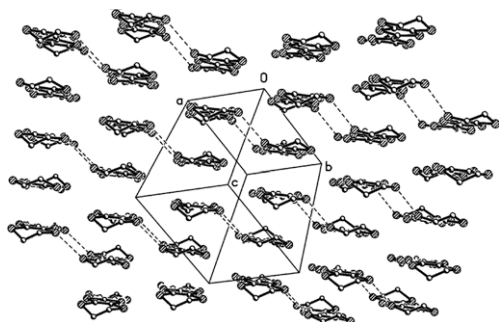


Fig. 9. Packing the BEDT-TTF cation radicals in  $(\text{BEDT-TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**3**).

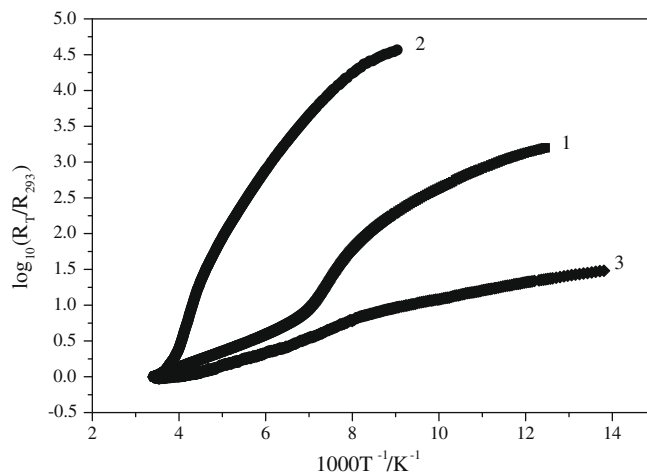


Fig. 10. The temperature dependence of resistance for the single crystals of  $(\text{BMDT-TTF})_4[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**1**),  $(\text{TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**2**) and polycrystalline  $(\text{BEDT-TTF})_2[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$  (**3**).

**Table 2**Tetrathiafulvalene-based radical cation salts of transition metal bis(dicarbollide) complexes  $[8,8'-XY-3,3'-M(1,2-C_2B_9H_{10})_2]^-$  of different stoichiometry.

Metal	Radical cation	Substituents (X, Y)			
		H, H	Br, Br	I, I (this work)	I, H
Co	TTF	1:1 [11]		1:1	
Fe	TTF	1:1 [18]			
Ni	TTF	1:1 [18]			
Cr	TTF	1:1 [18]			
Co	BMDT-TTF	1:1 [12]	4:1 [13]	4:1	
Co	BEDT-TTF	1:1 [11], 2:1 [12]	1:1 [13], 2:1 [13]	2:1	2:1 [12]
Cr	BEDT-TTF	2:1 [20]			
Co	TMTSF	2:1 [11]			
Fe	TMTSF	2:1 [12]			

the ethylene groups mounting to 0.94 Å. Both ethylene groups in the BEDT-TTF molecule are ordered and display eclipsed conformation.

Based on analysis of the intramolecular bond lengths in the BEDT-TTF radical cation [29], the charge on each BEDT-TTF radical cation in **3** has been assumed to be +0.5 that agrees well with the compound stoichiometry.

The geometry of the  $[8,8'-I_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$  anion in **3** is similar to those found in **1** and **2**. The dicarbollide ligands are mutually rotated by 180° producing *transoid* conformation. The distances from the cobalt atom to the  $C_2B_3$  planes are equal 1.49 Å. The average Co–C and Co–B bonds are 2.044 and 2.158 Å, respectively. The B–I bond length is 2.220(5) Å.

The electrical conductivity study of the tetrathiafulvalenium salts studied demonstrated that all they are semiconductors. The plots of temperature dependence of resistance for the single crystals of compounds **1–3** are presented in Fig. 10. The activation energy of **1**,  $E_a$ , was found to be 0.4 eV. The room temperature conductivity is  $5 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ , that is by a factor  $10^2$  higher than it was found for the TTF salt of the parent cobalt bis(dicarbollide) [12]. The activation energy of **2** equals  $E_a \approx 0.045$  eV and the room temperature conductivity  $\sigma_{293K}$  is  $0.25 \Omega^{-1} \text{cm}^{-1}$ , that is by a factor 4 lower than found in the case of the isostructural dibromo derivative [14]. The activation energy of **3** was found to be 0.03 eV. The room temperature conductivity  $\sigma_{293K}$  is  $6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ , that is by an order of magnitude greater than in the isostructural dibromo derivative [14] and significantly lower than in the moniodo derivative ( $\sigma_{293K} = 0.1 \Omega^{-1} \text{cm}^{-1}$ ) [13].

#### 4. Conclusions

Analysis of our own and available in the literature data on structure of tetrathiafulvalenium-based radical cation salts of the parent bis(1,2-dicarbollide) complexes of transition metals and their halogen derivatives (see Table 2) revealed the following regularities:

The most part of the parent bis(1,2-dicarbollide) complexes with the same radical cations ( $(\text{TTF})[3,3'-M(1,2-C_2B_9H_{11})_2]$ ,  $M = \text{Co, Fe, Ni}$ ;  $(\text{BEDT-TTF})_2[3,3'-M(1,2-C_2B_9H_{11})_2]$ ,  $M = \text{Co, Cr}$ ;  $(\text{TMTSF})_2[3,3'-M(1,2-C_2B_9H_{11})_2]$ ,  $M = \text{Co, Fe}$ ) are isostructural. A few exceptions (e.g.,  $(\text{TTF})[3,3'-\text{Cr}(1,2-C_2B_9H_{11})_2]$ ) are connected with different mutual orientation of the dicarbollide ligands producing *transoid*- and *cisoid*-rotational conformers with different dipole moments.

Substitution of hydrogen atoms for halogens in the dicarbollide ligands results in change of crystal structure of the radical cation salts even in the cases when the compound stoichiometry does not change.

All the studied tetrafulvalenium salts of the halogen substituted bis(dicarbollide) complexes with the same radical cations and having the same stoichiometry ( $(\text{BMDT-TTF})_4[8,8'-X_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ ,  $X = \text{Br, I}$ ;  $(\text{BEDT-TTF})_2[8,8'-XY-3,3'-Co(1,2-C_2B_9H_{10})_2]$ ,

$XY = \text{Br}_2, \text{I}_2, \text{HI}$ ) were found to be isostructural independently on the halogen atom. The bis(dicarbollide) anions in all these compounds have *transoid*-conformation.

Available at present data are still far to cover all field of conventional TTF derivatives and radical cation salt compositions, however these data are enough to predict crystal packing of many radical cation salts including bis(dicarbollide) complexes of transition metals and to design new molecular materials on their base. An additional study is necessary to establish effect of various metals and substituents in the dicarbollide ligands on electric and magnetic transport properties of this type of materials.

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#### Appendix A. Supplementary material

CCDC 700956, 700955 and 700954 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.03.035](https://doi.org/10.1016/j.jorganchem.2009.03.035).

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