

New fulvalenium salts of bis(dicarbollide) cobalt and iron: Synthesis, crystal structure and electrical conductivity

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Abstract

New radical cation salts (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (**2**), (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**) and (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (**4**) were synthesized and their crystal structures and electrical conductivities were determined. Compound **4** is isostructural to the earlier reported Co analogue. All the radical cation salts synthesized are semiconductors.

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Keywords: Molecular conductors; Cobalt bis(dicarbollide); Iron bis(dicarbollide); Bis(ethylenedithio)-tetrathiafulvalenium; Bis(methylenedithio)-tetrathiafulvalenium; Tetramethyltetraselenafulvalenium; Synthesis; Crystal structure; Electrical conductivity

1. Introduction

Over the past two decades a number of new organic superconductors and charge transfer salts with novel electrical and magnetic properties have been prepared based on bis(ethylenedithio)tetrathiafulvalene and its derivatives [1,2]. Crystal structure of fulvalene-based organic metals and superconductors is characterized by the presence of conducting radical cation layers alternating with anionic layers. The packing of radical cations in the crystal and conducting properties of the radical cation salts depend substantially on the type of anions involved. Only few conducting fulvalenium radical cation salts containing metallacarborane anions have been described up to date [3–6]. In this contribution, we describe synthesis of new

fulvalenium salts of cobalt- and ferracarboranes as well as the results of their X-ray structure and electric conductivity studies.

2. Results and discussion

(BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (**2**), (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**), and (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (**4**) crystals were synthesized by anodic oxidation of π -donors (bis(ethylenedithio)tetrathiafulvalene, bis(methylenedithio)-tetrathiafulvalene, and tetramethyltetraselenafulvalene, respectively) in the presence of the corresponding metallacarborane anions under galvanostatic conditions. 15-Crown-5 was used as additional component in the preparation of crystals **1** and **3** to increase solubility of the cobaltacarborane salt. In the first case this results in synthesis of the 2:1 salt **1**

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(synthesis of the corresponding 1:1 salt (BEDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] was reported earlier [6]), whereas in the second case only the 1:1 salt **3** was obtained independently on the cobaltacarborane concentration.

2.1. Crystal structure of (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**)

Crystal structure of **1** is formed by the BEDT-TTF radical cations on a general positions of a unit cell, and the [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ anions in a special centrosymmetric positions (Fig. 1). The structure differs strongly from the structure of the 1:1 complex (BEDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] described earlier [6], and has layered structure typical for electroconducting salts on the base of the BEDT-TTF cations and its derivatives with cationic and anionic layers alternate along the *c*-axis (Fig. 2). In conducting layer the BEDT-TTF radical cations are packed like β'-type [7] and form nearly regular stacks (Fig. 3). The intrastack S··S packing distances all are 3.77–3.80 Å that is greater than sum of van-der-Waals radii (3.68 Å) [8], whereas short interstack S··S contacts (3.41–3.51 Å) were found between the radical cations from neighbor stacks (Fig. 4). The BEDT-TTF cations are slightly bent, the maximum deviation of sulfur atoms from the cation plane being 0.12 Å and deviations of terminal carbon atoms mounting 1.08 Å. According to the empirical correlation between the central C–S and C=C bond lengths of BEDT-TTF and the partial oxidation state of BEDT-TTF in BEDT-TTF salts [9], the charge on each BEDT-TTF molecule is estimated to be +0.5, that is in accordance in the stoichiometry of the compound.

The Co–C and Co–B distances in **1** are 2.033(3)–2.057(4) Å and 2.064(4)–2.117(4) Å, respectively, and practical equivalentness of the Co–C(11) (2.057(4)) and Co–B(3) (2.064(4)) bond lengths (taking into account deviations) indicates possible disorder of boron and carbon

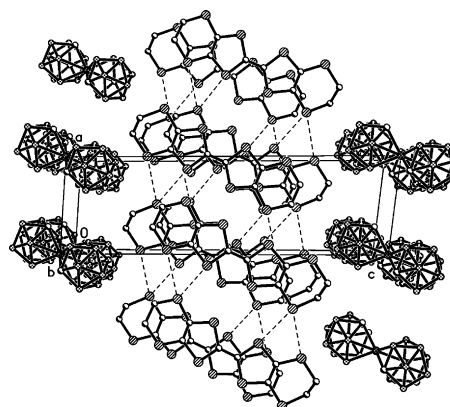


Fig. 2. A fragment of crystal structure of (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

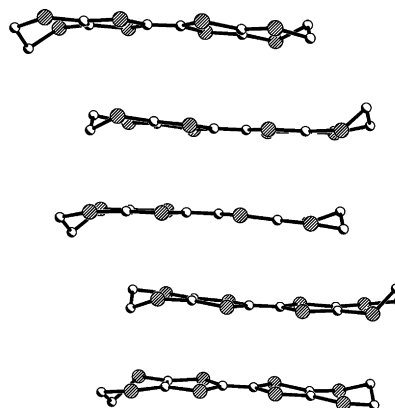


Fig. 3. A stack of BEDT-TTF radical cations in (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

atoms at the positions A(3) and C(11) with approximately equal occupancy. The C₂B₃ faces of the ligands are parallel as required by the crystallographic symmetry. The distances from the cobalt atom to the C₂B₃ planes are equal

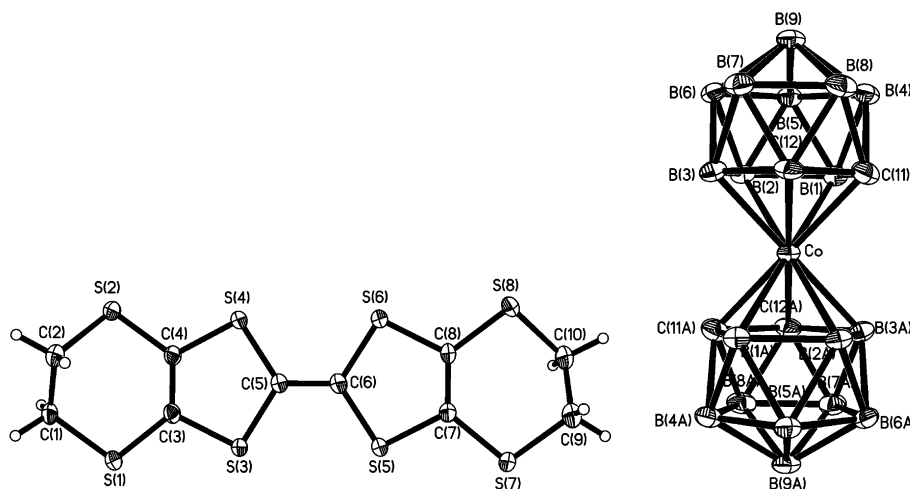


Fig. 1. Atomic designations in (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

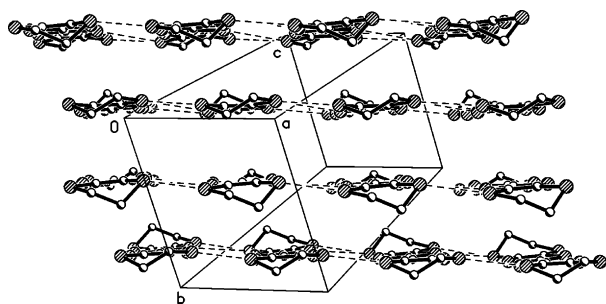


Fig. 4. Packing the BEDT-TTF cation radicals in $(\text{BEDT-TTF})_2[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

1.47 Å, that is typical for known salts of the cobalt bis(dicarbollide anion) [6,10].

2.2. Crystal structure of $(\text{BEDT-TTF})_2[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ (**2**)

Crystal structure of **2** is formed by the BEDT-TTF radical cations located at a general position of a unit cell, and the $[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ anions located at a special centrosymmetric position (Fig. 5). The BEDT-TTF cations and the cobaltacarborane anions are packed in stacks, forming conducting (cationic) and non-conducting (anionic) layers, that alternate along the *c*-axis (Fig. 6).

In the conducting layer the BEDT-TTF cations are packed like β -type [7] (Fig. 7), however stacks in **2** are irregular and contain dimer pairs with slightly shortened $\text{S}\cdots\text{S}$ contacts (3.643(3)–3.646(3) Å). The interplanar distances in the pairs were found to be 3.62 Å, whereas the interplanar distances between the pairs are 3.81 Å. Short interstack $\text{S}\cdots\text{S}$ contacts (3.540(3)–3.609(4) Å) were found between the radical cations from neighbor stacks (Figs. 7, 8). The BEDT-TTF cations are slightly bent, the maximum deviation of sulfur atoms from the cation plane being 0.17 Å and deviations of terminal carbon atoms mounting

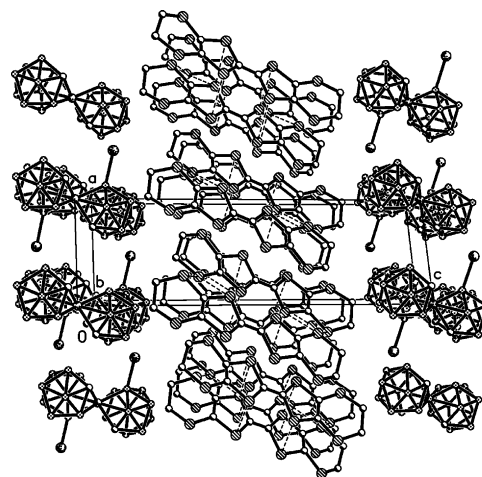


Fig. 6. A fragment of crystal structure of $(\text{BEDT-TTF})_2[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$.

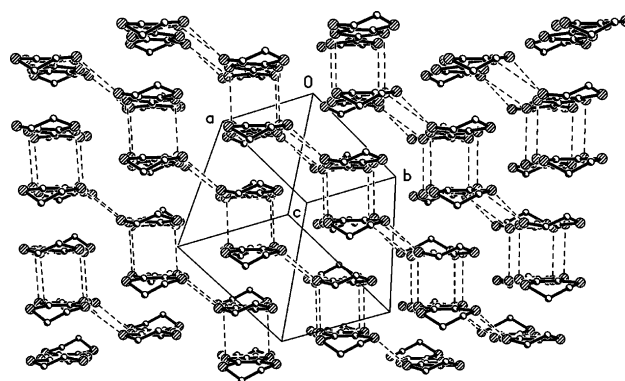


Fig. 7. Packing the BEDT-TTF cation radicals in $(\text{BEDT-TTF})_2[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

0.98 Å. Based on analysis of the intramolecular bond lengths in the BEDT-TTF radical cation [9] the charge on each BEDT-TTF radical cation in **2** has been assumed to be +0.5.

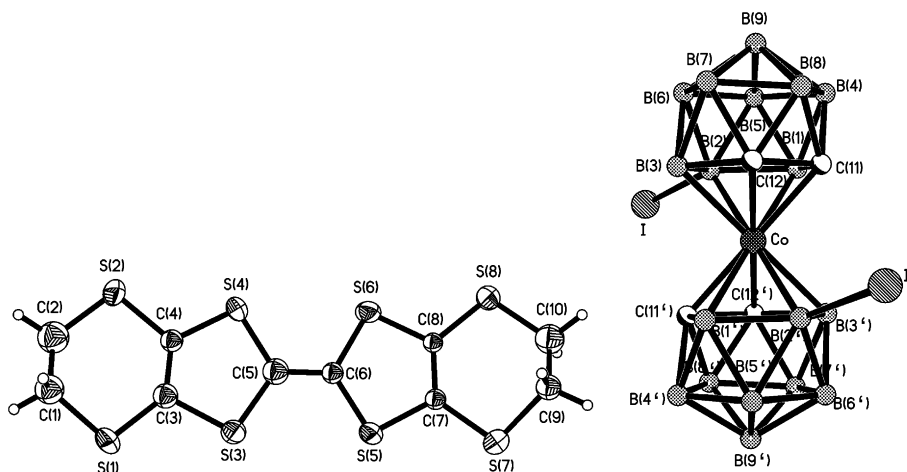


Fig. 5. Atomic designations in $(\text{BEDT-TTF})_2[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$.

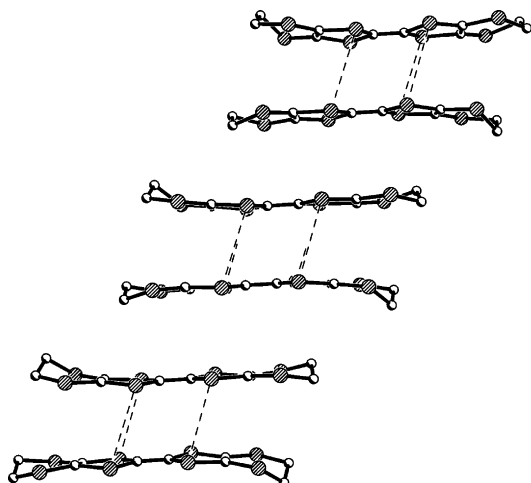


Fig. 8. A stack of BEDT-TTF radical cations in $(\text{BEDT-TTF})_2[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$.

The dicarbollide ligands in the cobaltacarborane anion are mutually rotated by 180°C producing an eclipsed orientation of the carborane cages (*transoid* conformation), similar to found in the structure of $\text{Cs}[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ [11]. The distances from the cobalt atom to the C_2B_3 planes are equal 1.48 Å, and the metal is approximately equidistant from the facial boron and carbon atoms although the Co–C distances are slightly shorter than the Co–B ones (mean values 2.011 and 2.118 Å, respectively). The C_2B_3 faces of the ligands are parallel as required by the crystallographic symmetry. The B–I distance (2.240(8) Å) is close to similar one found in $\text{Cs}[8\text{-I-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$ [11].

2.3. Crystal structure of $(\text{BMDT-TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ (3)

Crystal structure of **3** is formed by the BMDT-TTF radical cations and the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anions

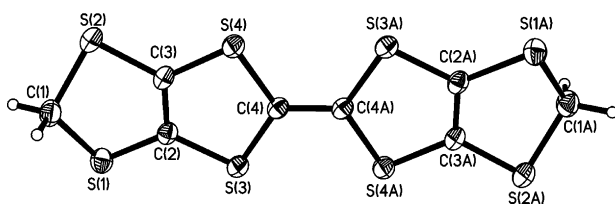


Fig. 9. Atomic designations in $(\text{BMDT-TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

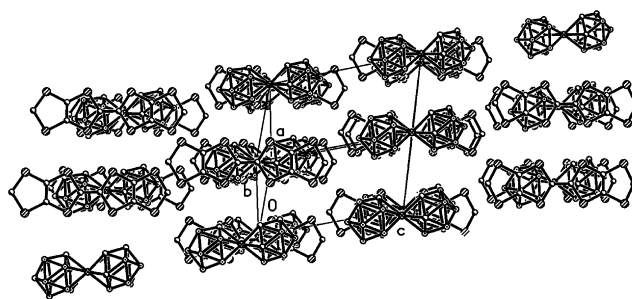


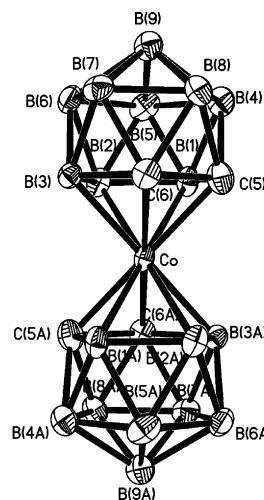
Fig. 10. A fragment of crystal structure of $(\text{BMDT-TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

located at a special centrosymmetric positions (Fig. 9). The BMDT-TTF cations and the cobaltacarborane anions alternate along the *ab* diagonal forming mixed stacks (Fig. 10). The radical cations are nearly planar, the maximum deviation of sulfur atoms from the cation plane being 0.06 Å and deviations of terminal carbon atoms mounting 0.57 Å.

The dicarbollide ligands in the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anion are mutually rotated by 180°C producing an eclipsed orientation of the carborane cages (*transoid* conformation). The C_2B_3 faces of the ligands are parallel as required by the crystallographic symmetry. The distances from the cobalt atom to the C_2B_3 planes are equal 1.48 Å, that is typical for known salts of the cobalt bis(dicarbollide anion) [6,10]. The Co–C and Co–B distances are 2.051(3)–2.056(4) and 2.074(3)–2.104(4) Å (mean values 2.054 and 2.087 Å, respectively).

2.4. Crystal structure of $(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ (4)

$(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ was found to be isostructural to the corresponding cobalt analogue $(\text{TMTSF})_2[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ [6]. Crystal structure of **4** is formed by the TMTSF radical cations on a general



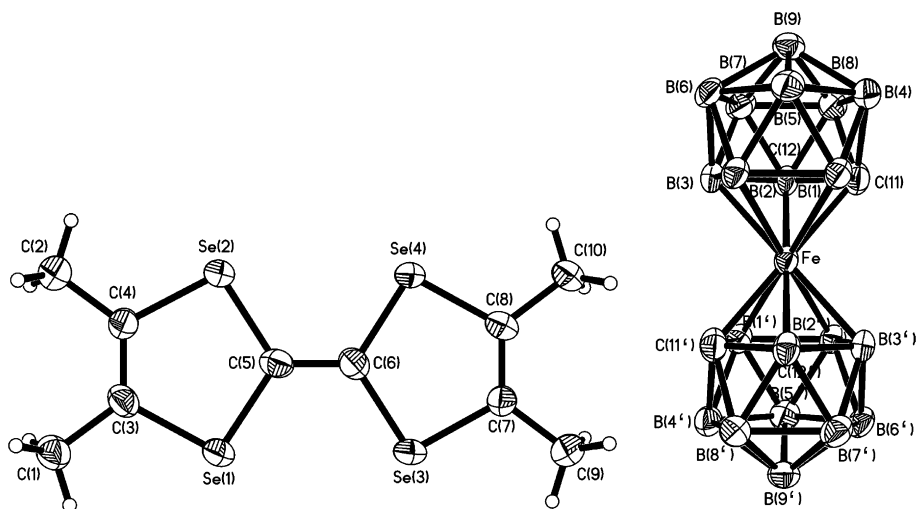


Fig. 11. Atomic designations in $(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

position of a unit cell and the $[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anions in a special centrosymmetric position (Fig. 11). The TMTSF cations and the $[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anions are packed in stacks along the a -axis, forming conducting (cationic) and non-conducting (anionic) layers, that are parallel to the basic ab - and ac -planes of the lattice and alternate along the b and c -axes (Fig. 12). The degree of overlapping the TMTSF radical cations is shown in Fig. 13. The distances between the TMTSF planes (drawn through Se and C atoms) are 3.81 and 3.77 Å, respectively, dihedral angle between these planes is 0° as imposed by symmetry (Fig. 14).

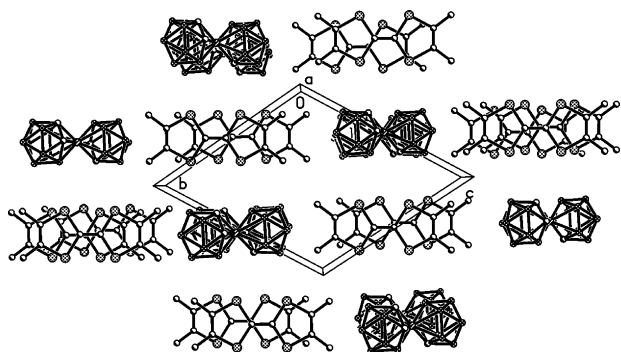


Fig. 12. A fragment of crystal structure of $(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

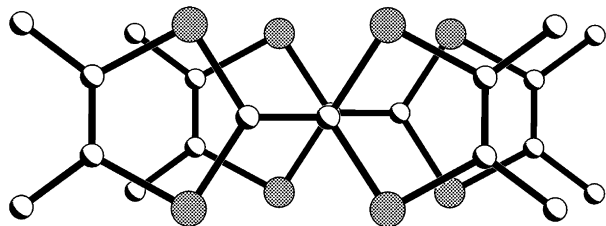


Fig. 13. Overlapping of TMTSF radical cations in the stack of the crystal structure of $(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

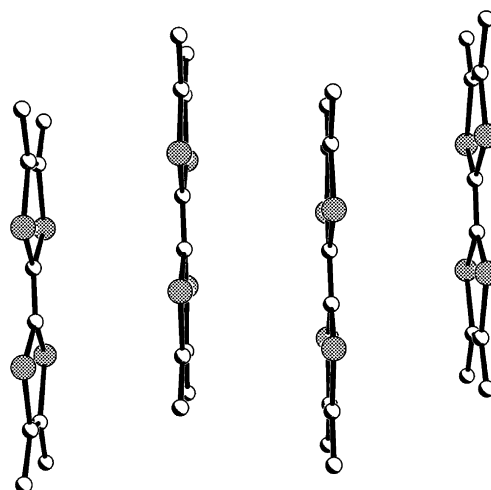


Fig. 14. A stack in $(\text{TMTSF})_2[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

The dicarbollide ligands in the $[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anion are mutually rotated by 180° producing an eclipsed orientation of the carborane cages (*transoid* conformation), similar to found in the structures of $(\text{Bu}_4\text{N})[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ and $(4\text{-MeC}_5\text{H}_4\text{NMe})[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ [12]. The C_2B_3 faces of the ligands are parallel as required by the crystallographic symmetry. The Fe–C and Fe–B distances are 2.075(3)–2.079(3) and 2.131(3)–2.157(4) Å (mean values 2.077 and 2.146 Å, respectively) and the distances from the iron atom to the C_2B_3 planes are equal 1.54 Å, that is typical for known salts of the iron bis(dicarbollide anion) [13].

2.5. Electrical conductivity and crystal structure peculiarities

The electrical conductivity study of the fulvalenium salts demonstrated that all they are semiconductors. The plots of temperature dependence of resistance for the single crystals of compounds 1–4 are presented in Figs. 15–18. The

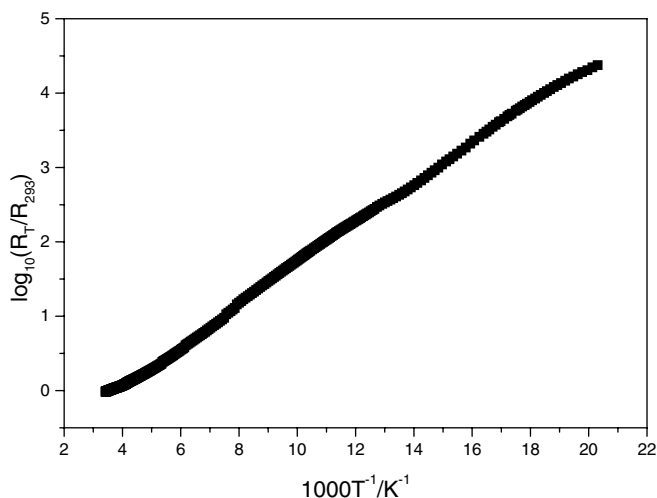


Fig. 15. The temperature dependence of resistance for the single crystal of (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

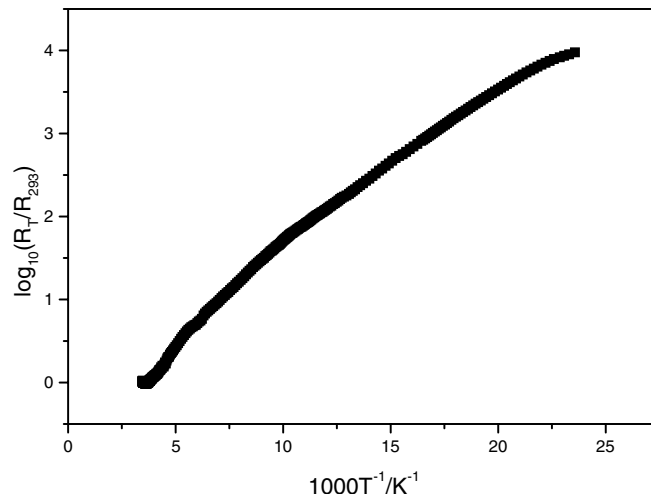


Fig. 18. The temperature dependence of resistance for the single crystal of (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂].

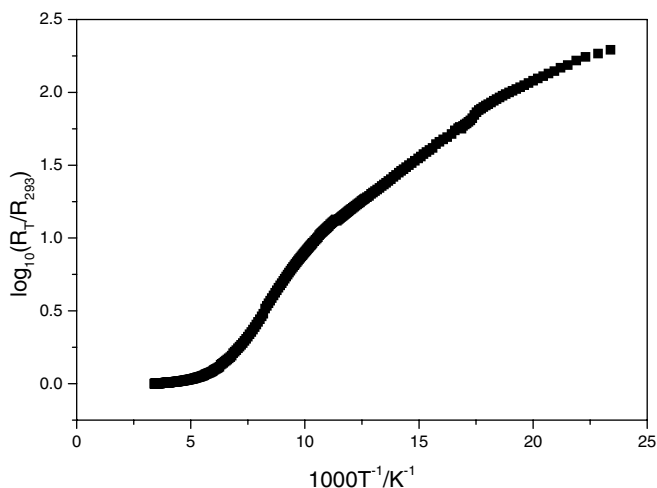


Fig. 16. The temperature dependence of resistance for the single crystal of (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)].

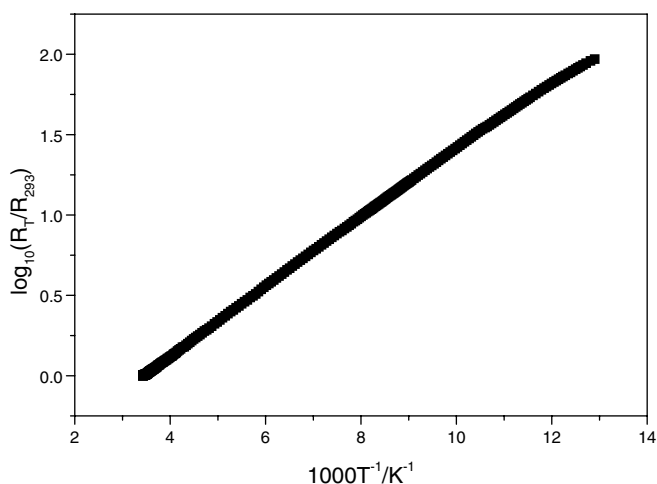


Fig. 17. The temperature dependence of resistance for the single crystal of (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

activation energies and room temperature conductivities of **1** and **2** having similar crystal packing (see Figs. 2 and 6) were found to be very close $E_a = 0.055$ and 0.050 eV and $\sigma_{293} = 0.1 \text{ Ohm}^{-1} \text{ cm}^{-1}$, respectively. The difference in the crystal packing **1** and **2** (β' and β type, respectively) arises probably from the difference in sizes of the anions. Taking to consideration that the iodine substituent in the cobaltacarborane anion in structure **2** is disordered between two dicarbollide ligands, one can assume that similar BEDT-TTF salt of the diiodo derivative of cobalt bis(dicarbollide) [8,8'-I₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ should have very close to structure **2** and belong to the same β type. Moreover, the anion size may be finely tuned by substituting the iodine for bromine or chlorine and the same structural type can be expected for other dihalogen derivatives [8,8'-X₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ (X = Cl, Br) as well. At present, BEDT-TTF is the most important organic donor molecule used in the preparation of new organic metals and superconductors. Most conducting and superconducting cation radical salts in the BEDT-TTF family form with a 2:1 donor:anion stoichiometry with monovalent anions. Many BEDT-TTF salts having β -type packing structural motif demonstrate metallic [14–16] or superconducting [17–19] properties. That is why we initiated synthesis of series of the BEDT-TTF salts with [8,8'-X₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ (X = Cl, Br, I) anions to study effect of the anion size on their structure and conductivity.

The activation energy of **3** equals $E_a \approx 0.04$ eV and the room temperature conductivity σ_{293} is $10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$. The low conductivity of **3** agrees well with the +1 charge on the BMDT-TTF cation radical assumed on the base of analysis of the intramolecular bond lengths. The central C=C bond in **3** is $1.401(6) \text{ \AA}$ that is close to that observed for other salts with the +1 charged BMDT-TTF cation radical [20–22]. Another criterion proposed by Nigrey et al. [21] is based on the ratio of the S··S distances of the outer(S_o)- and inner(S_i)-ring S atoms. The S_o/S_i ratio is

very sensitive to the charge of the BMDT-TTF cation radical and gives values of 1.014, 1.007, and 0.99 for the +1, +0.5, and zero-charged molecules. The S_0/S_i ratio for **3** is 1.015 that is very close to that of the +1-charged BMDT-TTF cation radical.

The electric conductivity study of the ferracarborane (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] revealed that **4** is semiconductor with the activation energy $E_a \approx 0.055$ eV and the room temperature conductivity $\sigma_{293} = 0.1 \text{ Ohm}^{-1} \text{ cm}^{-1}$ that differs significantly from the corresponding conductivity in the isostructural cobaltacarborane (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] ($\sigma = 15 \text{ Ohm}^{-1} \text{ cm}^{-1}$ [6]). The reason of this difference is not completely clear. It obviously cannot be explained by negligible difference in the anion size. As we noted earlier, the stoichiometry of **4** and its Co analogue is consistent both with (TMTSF^{0.5+})₂[3,3'-M^{III}(1,2-C₂B₉H₁₁)₂]⁻ and (TMTSF⁺)₂[3,3'-M^{II}(1,2-C₂B₉H₁₁)₂]²⁻ formulations. The first structure was supposed to be preferable for the Co compound based on its relatively high conductivity. Unfortunately, our attempts to find stronger arguments based on analysis of geometry of the TMTSF radical cation and the cobaltacarborane anion were unsuccessful. On the one hand, no relationship was found between charge of the TMTSF radical cation and bond lengths in a series of TMTSF salts of different stoichiometry, on the other hand, the conformation of the dicarbollide ligands in the cobaltacarborane anion does not give conclusive answer concerning the metal oxidation degree [6]. The geometry of the TMTSF radical cation in **4** is very close to one found in (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] [6] except some lengthening of the bridging C=C bond (1.378(6) and 1.35(1) Å). The dicarbollide ligands in the [3,3'-Fe(1,2-C₂B₉H₁₁)₂]⁻ anion in **4** were found to be in the

transoid conformation. The same conformation was found in the structures of (Bu₄N)[3,3'-Fe^{III}(1,2-C₂B₉H₁₁)₂] and (4-MeC₅H₄NMe)[3,3'-Fe^{III}(1,2-C₂B₉H₁₁)₂] [12], whereas the *cisoid* and *gauche* conformations were found in (TTF)-[3,3'-Fe^{III}(1,2-C₂B₉H₁₁)₂] [3] and [Fe^{III}Cp₂]⁺[3,3'-Fe^{III}(1,2-C₂B₉H₁₁)₂] [23], respectively. On the other hand, the *transoid* conformation was found in the compounds with the iron(II) bis(dicarbollide) anion – (Me₄N)₂[3,3'-Fe^{II}(1,2-C₂B₉H₁₁)₂] [24] and [Cp₂⁺ThMe]₂[3,3'-Fe^{II}(1,2-C₂B₉H₁₁)₂] [25]. These facts can be considered as an evidence of low barrier for the conformer interconversion in the [3,3'-Fe^{III}(1,2-C₂B₉H₁₁)₂]⁻ anion. Probably, the final decision on the metal oxidation degree in the ferracarborane anion and, as sequence, the charge of the TMTSF radical cations can be found from the analysis of distances from the iron atom to the C₂B₃ planes of the dicarbollide ligands. This distance in the structure of **4** is equal 1.54 Å, that is typical for known salts of the iron(III) bis(dicarbollide anion) [13], whereas in (Me₄N)₂[3,3'-Fe^{II}(1,2-C₂B₉H₁₁)₂] the corresponding distance is noticeable shorter and equals 1.48 Å [24], that is close to the one in the isoelectronic cobalt bis(dicarbollide) [3,3'-Co^{III}(1,2-C₂B₉H₁₁)₂]⁻ [6,10]. It means that both compound **4** and its Co analogue correspond to (TMTSF^{0.5+})₂[3,3'-M^{III}(1,2-C₂B₉H₁₁)₂]⁻ formulation.

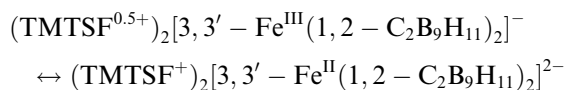
What is the reason of such significant difference in electric conductivity of these compounds having the same crystal structure? Probably, it can be explained by taking into account difference in electrochemical behavior of the metalacarborane anions. The M^{III}/M^{II} reduction potentials $E_{1/2}$ were found to be -0.424 and -1.42 V versus SCE for [3,3'-Fe(1,2-C₂B₉H₁₁)₂]⁻ and [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻, respectively [26]. The smaller reduction potential of the

Table 1

Crystal data and structure refinement for (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (**2**), (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**), (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (**4**)

Compound	(1)	(2)	(3)	(4)
Empiric formula	C ₂₄ H ₃₈ B ₁₈ CoS ₁₆	C ₂₄ H ₃₇ B ₁₈ CoIS ₁₆	C ₁₂ H ₂₆ B ₁₈ CoS ₈	C ₂₄ H ₄₆ B ₁₈ FeSe ₈
Formula weight	1093.01	1218.91	680.32	1216.72
Crystal system	Triclinic	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>P</i> $\bar{1}$ (No. 2)
<i>A</i> (Å)	6.626(2)	6.805(1)	6.7890(14)	7.5937(8)
<i>B</i> (Å)	8.015(2)	8.825(1)	9.5790(19)	12.256(1)
<i>C</i> (Å)	21.647(6)	21.074(1)	11.988(2)	13.026(1)
α (°)	84.84(1)	96.79 (1)	73.92(3)	116.715(5)
β (°)	83.61(2)	91.50(1)	78.04(3)	92.908(7)
γ (°)	76.33(2)	112.04(1)	78.36(3)	102.187(8)
<i>V</i> (Å ³)	1107.7(6)	1161.4(2)	724.1(3)	1043.6(2)
<i>Z</i>	1	1	1	1
λ (Å)	0.71073	1.5418	0.71073	1.5418
<i>D</i> _{calc.} (Mg m ⁻³)	1.64	1.74	1.56	1.94
μ (mm ⁻¹)	1.168	15.029	1.179	11.013
Number of reflections collected	4623	4040	2818	3585
Number of independent reflections	4623	3785	2581	3585
Number of reflections with [<i>F</i> ₀ > 4σ(<i>F</i> ₀)]	4005	1015	1975	2020
Number of parameters refined	268	172	178	233
(2θ) _{max} (°)	54.00	51.00	130.04	139.62
<i>R</i>	0.057	0.091	0.072	0.042

ferracarborane allows us to suppose a formation of some amount of iron(II) species according to equilibrium



This process increases formal average charge on the TMTSF species due to partial oxidation of the neutral TMTSF molecules to the radical cations or/and the radical cations to the dications (the oxidation potentials $E(1)_{1/2} = 0.37$ V and $E(2)_{1/2} = 0.67$ versus SCE, respectively [27]). Naturally, this point needs more strong justification including further synthesis of a series of isostuctural and isomorphous charge transfer salts of these metallacarborane anions.

3. Conclusion

New radical cation salts (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (1), (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)-(1',2'-C₂B₉H₁₁)] (2), (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (3) and (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (4) were synthesized and their crystal structures and electrical conductivities were determined. Compounds 1, 2 and 4 have layered structures with conducting stacks of fulvalenium radical cations. Compound 4 is isostructural to the earlier reported Co analogue (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂]. All the radical cation salts synthesized were found to be semiconductors. The room temperature conductivity of crystals 1, 2, and 4 equal 0.1 Ohm⁻¹ cm⁻¹, whereas for crystal 3 its value is 0.01 Ohm⁻¹ cm⁻¹.

4. Experimental

4.1. Synthesis

BEDT-TTF, BMDT-TTF and TMTSF (Aldrich) were used as received. Na[3,3'-Co(1,2-C₂B₉H₁₁)₂], (Me₃NH)[8-I-3,3'-Co(1,2-C₂B₉H₁₀)-(1',2'-C₂B₉H₁₁)] and (Me₃NH)[3,3'-Fe(1,2-C₂B₉H₁₁)₂] were prepared by the literature methods [26,28]. The crystals were grown by electrochemical crystallization under argon atmosphere in standard two-electrode H-cell with platinum electrodes separated by glass frit under galvanostatic conditions [29]. To prepare high-quality monocrystals a current applied was changed discretely on 0.05 mA per day from 0.10 to 1.00 mA. The period of crystal growth was 3–5 weeks. Since all the cation radical salts were prepared by anodic oxidation the composition of solution in the cathodic compartment of the H-cell was not investigated. All the parameters of the electrosyntheses were digitally controlled.

Crystals of 1 were obtained from the Na[3,3'-Co(1,2-C₂B₉H₁₁)₂] (2 × 10⁻² mol/l)–15-crown-5 (3 × 10⁻² mol/l)–BEDT-TTF (2 × 10⁻³ mol/l) system using 1,2,2-trichloroethane or dichloromethane as a solvent.

Crystals of 2 were obtained from the (Me₃NH)[8-I-3,3'-Co(1,2-C₂B₉H₁₀)-(1',2'-C₂B₉H₁₁)] (8 × 10⁻³ mol/l) – BEDT-

TTF (2 × 10⁻³ mol/l) system using 1,1,2-trichloroethane or dichloromethane as a solvent.

Crystals of 3 were obtained from the Na[3,3'-Co(1,2-C₂B₉H₁₁)₂] (1 × 10⁻²–2 × 10⁻² mol/l) – 15-crown-5 (3 × 10⁻² mol/l) – BMDT-TTF (2 × 10⁻³ mol/l) system using 1,1,2-trichloroethane, 1,2-dichloroethane, or dichloromethane as a solvent.

Crystals of 4 were obtained from the (Me₃NH)[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (8 × 10⁻³ mol/l) – TMTSF (2 × 10⁻³ mol/l) system in 1,1,2-trichloroethane.

Table 2

Selected bond distances and bond angles for (BEDT-TTF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (1)

BEDT-TTF radical cation			
Bond length	<i>d</i> (Å)		
C(5)–C(6)	1.365(5)	C(3)–S(1)	1.741(4)
C(5)–S(3)	1.740(4)	C(4)–S(2)	1.751(4)
C(5)–S(4)	1.728(4)	C(7)–S(7)	1.741(4)
C(6)–S(5)	1.731(4)	C(8)–S(8)	1.744(4)
C(6)–S(6)	1.748(4)	S(1)–C(1)	1.809(4)
S(3)–C(3)	1.746(4)	S(2)–C(2)	1.812(4)
S(4)–C(4)	1.743(4)	S(7)–C(9)	1.774(5)
S(5)–C(7)	1.743(4)	S(8)–C(10)	1.800(5)
S(6)–C(8)	1.753(4)	C(1)–C(2)	1.512(6)
C(3)–C(4)	1.340(5)	C(9)–C(10)	1.475(7)
C(7)–C(8)	1.338(6)		
Bond angle	ω (°)		
S(3)–C(5)–S(4)	115.5(2)	S(4)–C(4)–S(2)	116.0(2)
S(5)–C(6)–S(6)	114.8(2)	S(5)–C(7)–S(7)	113.0(2)
C(6)–C(5)–S(3)	121.5(3)	S(6)–C(8)–S(8)	116.1(2)
C(6)–C(5)–S(4)	123.0(3)	C(4)–C(3)–S(1)	129.0(3)
C(5)–C(6)–S(5)	123.2(3)	C(3)–C(4)–S(2)	125.7(3)
C(5)–C(6)–S(6)	122.0(3)	C(8)–C(7)–S(7)	129.1(3)
C(5)–S(3)–C(3)	95.3(2)	C(7)–C(8)–S(8)	127.5(3)
C(5)–S(4)–C(4)	94.7(2)	C(3)–S(1)–C(1)	104.0(2)
C(6)–S(5)–C(7)	95.3(2)	C(4)–S(2)–C(2)	98.1(2)
C(6)–S(6)–C(8)	95.3(2)	C(7)–S(7)–C(9)	103.7(2)
S(3)–C(3)–C(4)	116.1(3)	C(8)–S(8)–C(10)	99.4(2)
S(4)–C(4)–C(3)	118.2(3)	S(1)–C(1)–C(2)	116.0(3)
S(5)–C(7)–C(8)	117.9(3)	S(2)–C(2)–C(1)	112.2(3)
S(6)–C(8)–C(7)	116.3(3)	S(7)–C(9)–C(10)	115.3(3)
S(3)–C(3)–S(1)	114.9(2)	S(8)–C(10)–C(9)	116.6(4)
[3,3'-Co(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻			
Bond length	<i>d</i> (Å)		
Co–C(11)	2.057(4)	B(3)–B(7)	1.756(6)
Co–C(12)	2.033(3)	B(1)–B(5)	1.789(6)
Co–B(1)	2.117(4)	B(3)–B(6)	1.734(6)
Co–B(3)	2.064(4)	B(2)–B(5)	1.773(6)
Co–B(2)	2.116(4)	B(2)–B(6)	1.769(6)
C(11)–C(12)	1.679(6)	B(4)–B(8)	1.780(7)
C(11)–B(1)	1.743(6)	B(7)–B(8)	1.768(7)
C(12)–B(3)	1.671(6)	B(4)–B(5)	1.763(6)
B(1)–B(2)	1.786(6)	B(6)–B(7)	1.767(7)
B(2)–B(3)	1.733(6)	B(5)–B(6)	1.765(6)
C(11)–B(8)	1.751(6)	B(8)–B(9)	1.776(6)
C(12)–B(8)	1.724(6)	B(4)–B(9)	1.769(7)
C(11)–B(4)	1.747(6)	B(7)–B(9)	1.774(7)
C(12)–B(7)	1.723(6)	B(5)–B(9)	1.769(6)
B(1)–B(4)	1.777(6)	B(6)–B(9)	1.783(6)

4.2. Electrical resistivity measurements

The temperature dependence of electric resistivity was measured on single crystals using standard dc-four-probe technique. The crystals preliminary were glued on the module with 4 platinum thin wire of diameter 15 μm with the aid of conducting graphite paint. The module was mounted inside of stainless-steel light-wall tube (diameter ~ 11 mm), and the tube was slowly inserted to the transport helium jar with gradual cooling of the sample from 293 K to 4.2 K with cooling rate of 50–60 K/h.

Table 3
Selected bond distances and bond angles for (BEDT-TTF)₂[8-I-3,3'-Co(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (2)

BEDT-TTF radical cation			
Bond length	<i>d</i> (Å)		
C(5)–C(6)	1.36(1)	C(3)–S(1)	1.702(9)
C(5)–S(3)	1.761(9)	C(4)–S(2)	1.771(8)
C(5)–S(4)	1.75(10)	C(7)–S(7)	1.747(8)
C(6)–S(5)	1.698(8)	C(8)–S(8)	1.746(8)
C(6)–S(6)	1.741(8)	S(1)–C(1)	1.78(1)
S(3)–C(3)	1.811(9)	S(2)–C(2)	1.78(1)
S(4)–C(4)	1.719(8)	S(7)–C(9)	1.807(9)
S(5)–C(7)	1.748(8)	S(8)–C(10)	1.77(1)
S(6)–C(8)	1.723(8)	C(1)–C(2)	1.44(1)
C(3)–C(4)	1.31(1)	C(9)–C(10)	1.44(1)
C(7)–C(8)	1.37(1)		
Bond angle	ω (°)		
S(3)–C(5)–S(4)	113.2(5)	S(4)–C(4)–S(2)	113.4(5)
S(5)–C(6)–S(6)	117.4(4)	S(5)–C(7)–S(7)	116.3(5)
C(6)–C(5)–S(3)	123.8(7)	S(6)–C(8)–S(8)	114.9(4)
C(6)–C(5)–S(4)	122.9(7)	C(4)–C(3)–S(1)	134.2(7)
C(5)–C(6)–S(5)	123.0(7)	C(3)–C(4)–S(2)	123.8(6)
C(5)–C(6)–S(6)	119.6(7)	C(8)–C(7)–S(7)	127.4(6)
C(5)–S(3)–C(3)	96.4(4)	C(7)–C(8)–S(8)	127.5(6)
C(5)–S(4)–C(4)	95.1(4)	C(3)–S(1)–C(1)	100.6(4)
C(6)–S(5)–C(7)	94.5(4)	C(4)–S(2)–C(2)	103.9(5)
C(6)–S(6)–C(8)	93.8(4)	C(7)–S(7)–C(9)	97.6(4)
S(3)–C(3)–C(4)	112.0(6)	C(8)–S(8)–C(10)	104.6(4)
S(4)–C(4)–C(3)	122.7(7)	S(1)–C(1)–C(2)	120.9(6)
S(5)–C(7)–C(8)	116.2(6)	S(2)–C(2)–C(1)	117.5(7)
S(6)–C(8)–C(7)	117.5(6)	S(7)–C(9)–C(10)	118.2(6)
S(3)–C(3)–S(1)	112.8(5)	S(8)–C(10)–C(9)	116.5(7)
[8-I-3,3'-Co(1,2-C ₂ B ₉ H ₁₀)(1',2'-C ₂ B ₉ H ₁₁)] ⁺			
Bond length	<i>d</i> (Å)		
Co–C(11)	2.022(7)	B(3)–B(7)	1.84(1)
Co–C(12)	2.000(8)	B(1)–B(5)	1.75(1)
Co–B(1)	2.15(1)	B(3)–B(6)	1.78(1)
Co–B(3)	2.11(10)	B(2)–B(5)	1.81(1)
Co–B(2)	2.085(9)	B(2)–B(6)	1.74(1)
B(2)–I	2.240(8)	B(4)–B(8)	1.88(2)
C(11)–C(12)	1.66(1)	B(7)–B(8)	1.76(1)
C(11)–B(1)	1.65(1)	B(4)–B(5)	1.71(1)
C(12)–B(3)	1.71(1)	B(6)–B(7)	1.83(1)
B(1)–B(2)	1.79(1)	B(5)–B(6)	1.77(2)
B(2)–B(3)	1.73(1)	B(8)–B(9)	1.75(2)
C(11)–B(8)	1.71(1)	B(4)–B(9)	1.77(2)
C(12)–B(8)	1.69(1)	B(7)–B(9)	1.75(2)
C(11)–B(4)	1.76(1)	B(5)–B(9)	1.81(2)
C(12)–B(7)	1.72(1)	B(6)–B(9)	1.82(1)
B(1)–B(4)	1.71(1)		

4.3. X-ray diffraction analysis

X-ray diffraction studies of **1** and **3** were carried out with a Bruker-P4 diffractometer, using graphite monochromated Mo K α radiation (ω -scanning), whereas X-ray diffraction studies of **2** and **4** were performed on an Enraf Nonius CAD-4 diffractometer, using graphite monochromated Cu K α radiation (ω -scanning). The structures were solved by direct methods followed by Fourier difference synthesis using the SHELXS software [30]. The structures of **1**, **3**, and **4** were refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms using SHELXL software [31]. The structure of **2** was refined by the full-matrix least-squares method in anisotropic approximation for the Co, I, and S atoms, the C and B atoms were refined isotropically due to insufficient number of reflections caused by poor diffractivity of the crystal. The reflection intensities were corrected for absorption using semi-empirical method [32]. The hydrogen atoms in structure of **2** were determined from the geometry conditions. The occupancy of the iodine atom in the structure of **2** is equal 0.5.

Table 4
Selected bond distances and bond angles for (BMDT-TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (3)

BMDT-TTF radical cation			
Bond length	<i>d</i> (Å)		
C(4)–C(4A)	1.401(6)	C(2)–C(3)	1.368(5)
C(4)–S(3)	1.723(4)	C(2)–S(1)	1.747(3)
C(4)–S(4)	1.732(3)	C(3)–S(2)	1.737(3)
S(3)–C(2)	1.723(3)	S(1)–C(1)	1.821(4)
S(4)–C(3)	1.714(4)	S(2)–C(1)	1.825(4)
Bond angle	ω (°)		
S(3)–C(4)–S(4)	115.8(2)	S(3)–C(2)–S(1)	125.8(2)
C(4A)–C(4)–S(3)	123.2(3)	S(4)–C(3)–S(2)	125.2(2)
C(4A)–C(4)–S(4)	120.9(3)	C(3)–C(2)–S(1)	117.3(2)
C(4)–S(3)–C(2)	95.1(2)	C(2)–C(3)–S(2)	117.5(3)
C(4)–S(4)–C(3)	95.1(2)	C(2)–S(1)–C(1)	91.9(2)
C(3)–C(2)–S(3)	116.8(3)	C(3)–S(2)–C(1)	91.9(2)
C(2)–C(3)–S(4)	117.1(2)	S(1)–C(1)–S(2)	109.2(2)
[3,3'-Co(1,2-C ₂ B ₉ H ₁₁) ₂] ⁺			
Bond length	<i>d</i> (Å)		
Co–C(5)	2.056(4)	B(3)–B(7)	1.754(6)
Co–C(6)	2.051(3)	B(1)–B(5)	1.737(5)
Co–B(1)	2.084(4)	B(3)–B(6)	1.742(5)
Co–B(3)	2.074(3)	B(2)–B(5)	1.782(6)
Co–B(2)	2.104(4)	B(2)–B(6)	1.792(6)
C(5)–C(6)	1.699(5)	B(4)–B(8)	1.755(5)
C(5)–B(1)	1.689(5)	B(7)–B(8)	1.768(6)
C(6)–B(3)	1.690(5)	B(4)–B(5)	1.768(6)
B(1)–B(2)	1.734(5)	B(6)–B(7)	1.767(6)
B(2)–B(3)	1.754(5)	B(5)–B(6)	1.776(6)
C(5)–B(8)	1.739(5)	B(8)–B(9)	1.765(5)
C(6)–B(8)	1.766(5)	B(4)–B(9)	1.761(5)
C(5)–B(4)	1.742(5)	B(7)–B(9)	1.782(5)
C(6)–B(7)	1.750(5)	B(5)–B(9)	1.794(6)
B(1)–B(4)	1.737(6)	B(6)–B(9)	1.803(7)

Table 5
Selected bond distances and bond angles for (TMTSF)₂[3,3'-Fe(1,2-C₂B₉H₁₁)₂] (4)

TMTSF radical cation			
Bond length		<i>d</i> (Å)	
C(5)–C(6)	1.378(6)	Se(4)–C(8)	1.889(4)
C(5)–Se(1)	1.876(3)	C(3)–C(4)	1.351(4)
C(5)–Se(2)	1.878(3)	C(7)–C(8)	1.348(4)
C(6)–Se(3)	1.864(3)	C(1)–C(3)	1.508(5)
C(6)–Se(4)	1.869(3)	C(2)–C(4)	1.477(5)
Se(1)–C(3)	1.894(4)	C(7)–C(9)	1.498(5)
Se(2)–C(4)	1.895(3)	C(8)–C(10)	1.513(5)
Se(3)–C(7)	1.894(3)		
Bond angle		ω (°)	
Se(1)–C(5)–Se(2)	114.2(2)	Se(23)–C(4)–C(3)	117.9(3)
Se(3)–C(6)–Se(4)	115.0(2)	Se(3)–C(7)–C(8)	118.5(3)
Se(1)–C(5)–C(6)	122.9(2)	Se(4)–C(8)–C(7)	118.4(3)
Se(2)–C(5)–C(6)	122.8(2)	Se(1)–C(3)–C(1)	114.6(2)
Se(3)–C(6)–C(5)	122.7(2)	Se(2)–C(4)–C(2)	115.5(2)
Se(4)–C(6)–C(5)	122.1(2)	Se(3)–C(7)–C(9)	114.8(2)
C(3)–Se(1)–C(5)	94.3(1)	Se(40)–C(8)–C(10)	115.0(2)
C(4)–Se(2)–C(5)	94.6(1)	C(1)–C(3)–C(4)	126.5(3)
C(6)–Se(3)–C(7)	94.0(1)	C(2)–C(4)–C(3)	126.5(3)
C(6)–Se(4)–C(8)	94.1(1)	C(8)–C(7)–C(9)	126.7(3)
Se(1)–C(3)–C(4)	118.8(3)	C(7)–C(8)–C(10)	126.6(3)
[3,3'-Fe(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻			
Bond length		<i>d</i> (Å)	
Fe–C(11)	2.079(3)	B(3)–B(7)	1.730(6)
Fe–C(12)	2.075(3)	B(1)–B(5)	1.765(5)
Fe–B(1)	2.150(4)	B(3)–B(6)	1.723(6)
Fe–B(3)	2.131(3)	B(2)–B(5)	1.778(6)
Fe–B(2)	2.157(4)	B(2)–B(6)	1.784(6)
C(11)–C(12)	1.613(4)	B(4)–B(8)	1.765(6)
C(11)–B(1)	1.723(6)	B(7)–B(8)	1.777(5)
C(12)–B(3)	1.678(4)	B(4)–B(5)	1.782(5)
B(1)–B(2)	1.807(4)	B(6)–B(7)	1.752(6)
B(2)–B(3)	1.736(6)	B(5)–B(6)	1.769(5)
C(11)–B(8)	1.712(6)	B(8)–B(9)	1.751(6)
C(12)–B(8)	1.715(5)	B(4)–B(9)	1.763(5)
C(11)–B(4)	1.729(6)	B(7)–B(9)	1.778(6)
C(12)–B(7)	1.703(5)	B(5)–B(9)	1.789(6)
B(1)–B(4)	1.780(6)	B(6)–B(9)	1.791(5)

Details of the data collection, structure solution and refinement are listed in Table 1. Selected bond distances and angles are presented in Tables 2–5.

5. Supplementary material

CCDC 637459, 637460, 637458 and 637461 contain the supplementary crystallographic data for **1**, **2**, **3** and **2b**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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