

Synthesis, structure and electrical conductivity of fulvalenium salts of cobalt bis(dicarbollide) anion

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Abstract

New radical cation salts (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**2**) and (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**) were synthesized and their crystal structures and electrical conductivities were determined. Compound **1** has layered structure with conducting stacks of the TMTSF cations, whereas compounds **2** and **3** contain separated pairs of fulvalenium cations. Conductivity of crystals **1** at room temperature was found to be 15 Ohm⁻¹ cm⁻¹, that is the maximum value found for fulvalenium metallacarborane salts. © 2006 Elsevier B.V. All rights reserved.

Keywords: Cobalt bis(dicarbollide); Tetramethyltetraselenafulvalenium; Tetrathiafulvalenium; Bis(ethylenedithio)-tetrathiafulvalenium; Synthesis; Crystal structure; Electrical conductivity

1. Introduction

The majority of known organic conductors and superconductors are radical cation salts based on bis(ethylenedithio)tetrathiafulvalene (ET) and its derivatives containing anionic complexes of different metals [1]. The tetrathiafulvalene-based organic metals and superconductors are quasi-two-dimensional systems with layered topology. Their crystal structure is characterized by the presence of conducting radical cation layers alternating with anionic layers. The packing of the radical cations in the crystal and the properties of the radical cation salts depend substantially on the type of anions involved. The search for organic superconductors with high temperature of transition to the superconducting state remains an interest for

synthetic chemists, and the variation of the anionic component can be one of the approaches to achieve this goal.

A few conducting radical cation salts containing metallacarborane anions have been described up to date [2–4]. All these salts are based on iron, nickel, and chromium bis(dicarbollide) anions, and no radical cation salt derived from the cobalt bis(dicarbollide) anion [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻, the most studied metallacarborane [5], was reported. The cobalt bis(dicarbollide) anion and its derivatives are of interest for extraction of radionuclides from radioactive waste [6–8], as components of ion-selective electrodes [9,10], weakly-coordinating anions [11], for synthesis of agents for boron neutron capture therapy [12–14], radionuclide diagnostics [15], and HIV protease inhibitors [16]. In this contribution, we describe the syntheses of tetramethyltetraselenafulvalenium, tetrathiafulvalenium, and bis(ethylenedithio)-tetrathiafulvalenium salts of the cobalt bis(dicarbollide) anion as well as the results of their X-ray structure and electric conductivity studies.

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2. Results and discussion

(TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (TTF)[3,3'-Co(1,2-C₂B₉C₂H₁₁)₂] (**2**), and (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**) crystals, were synthesized by anodic oxidation of the corresponding π -donors (tetramethyltetraselenafulvalene, tetrathiafulvalene, and bis(ethylenedithio)tetrathiafulvalene, respectively) in the presence of Na[3,3'-Co(1,2-B₉C₂H₁₁)₂] under galvanostatic conditions. Our attempts to prepare the similar compound with tetramethyltetrathiafulvalene (TMTTF) under similar conditions failed. Crystal structures and electrical conductivities of the fulvalenium salt **1–3** were determined.

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

Crystal structure of **1** is formed by the TMTSF radical cations on a general position of a unit cell, and the [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ anions in a special centrosymmetric position (Fig. 1). The TMTSF cations and the [3,3'-Co(1,2-C₂B₉H₁₁)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. 2). The degree of overlapping the TMTSF radical cations is shown in Fig. 3. The neighboring molecules are slipped in respect to each along the C=C bond. The distances between the TMTSF planes (drawn through Se and C atoms) are 3.80 and 3.76 Å, dihedral angle between these planes is 0° as imposed by symmetry (Fig. 4). The intermolecular Se...Se distances in the stacks are beyond the sum of van-der-Waals radii. No shortened cation...anion distance was found. The TMTSF cations are practically planar, the dihedral angle between average planes of the five-membered heterocycles (drawn through all non-hydrogen atoms) being 0.4°.

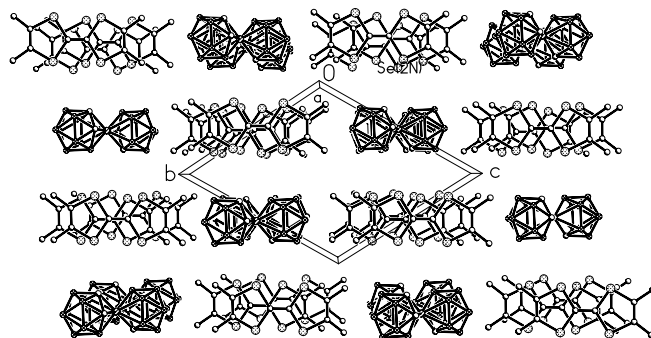


Fig. 2. A fragment of crystal structure of (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

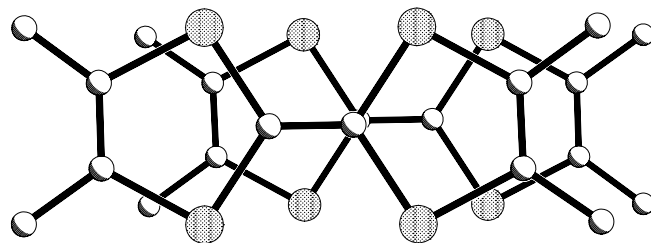


Fig. 3. Overlapping of TMTSF radical cations in the stack of the crystal structure of (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

The cobalt bis(dicarbollide) anion consists of two dicarbollide units sandwiched around a cobalt atom ion with the C₂B₃ faces of the two ligands which are nearly parallel. The dicarbollide ligands are mutually rotated by 180° producing an eclipsed orientation of the carborane cages (*transoid* conformation), similar to that found in the structure of [Cs(DME)₄]₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] [17]. The distances from the cobalt atom to the C₂B₃ planes are equal 1.46 Å, and the metal is approximately equidistant from the facial boron and carbon atoms although the Co–C

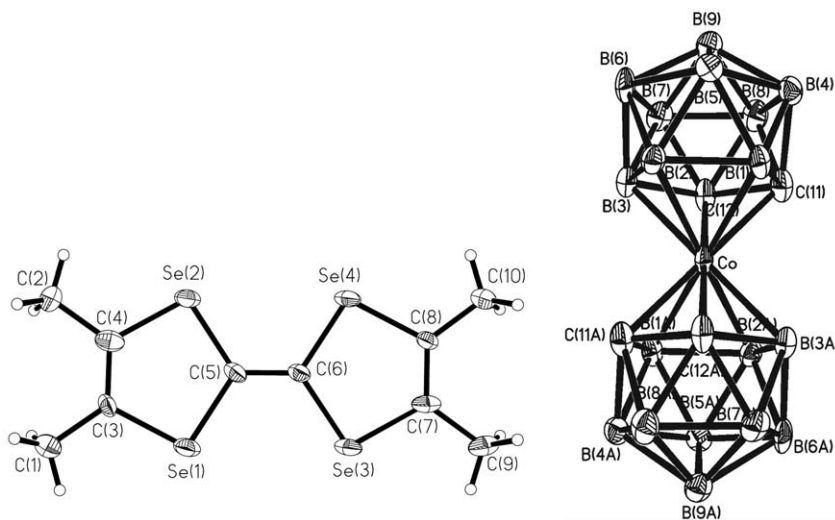


Fig. 1. Atomic designations in (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

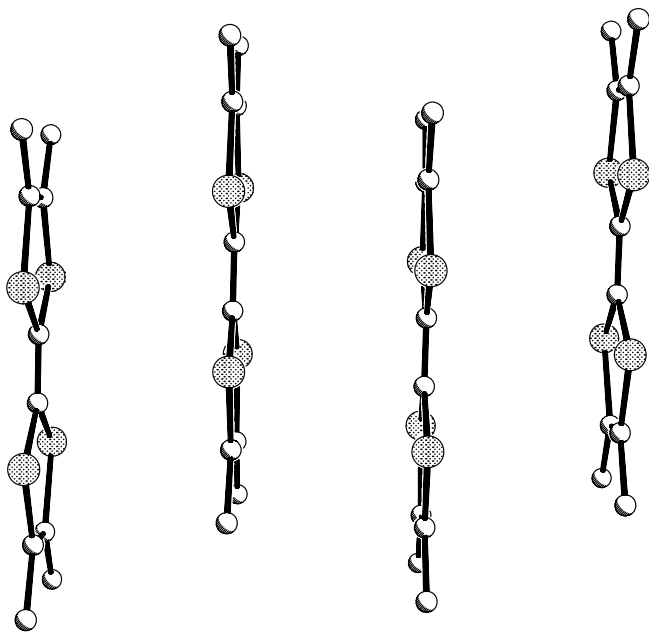


Fig. 4. A stack in $(\text{TMTSF})_2[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

distances are slightly shorter than the Co–B ones (mean values 2.030 and 2.100 Å, respectively).

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

$(\text{TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ was found to be isostructural to the corresponding iron and nickel analogues $(\text{TTF})[3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ and $(\text{TTF})[3,3'\text{-Ni}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ [2]. Crystal structure of **2** is formed by the TTF cations and the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anions on general positions of the cell unit (Fig. 5). Unlike to most of radical cation conductors, the structure of $(\text{TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ is not composed of stacks in layers

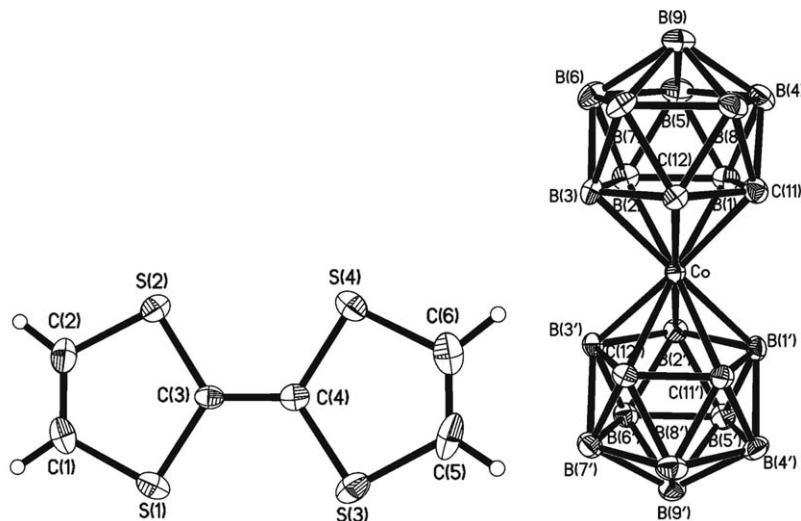


Fig. 5. Atomic designations in $(\text{TTF})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$.

(Fig. 6). The TTF radical cations form pairs bonded by an inversion center. The anions are situated as on a chess-board between the cation pairs. The radical cations in pairs are fully eclipsed (Fig. 7). The distances between the TTF planes are 3.44 Å, dihedral angle between these planes being 0° on symmetry conditions. Shortened intermolecular S...S distances ($3.353(1) + 3.449(1)$ Å) were found in the TTF pairs (sum of van-der-Waals radii is 3.68 Å [18]). There is no intermolecular interaction between the TTF pairs. The TTF cations in the structure of **2** are less flat than the TMTSF cations in **1**, dihedral angle between the planes of the five-member cycles being 3.5° .

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 36° producing a staggered orientation of the carborane cages (*cisoid* conformation), similar to that found in the structure of $(\text{Et}_3\text{NH})[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ [19]. The C_2B_3 faces of the ligands are nearly parallel (the dihedral angle is 3.8°). The distances from the cobalt atom to the C_2B_3 planes are equal 1.47 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 2.044 and 2.089 Å, respectively).

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

Crystal structure of **3** is formed by the ET cations and the $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anions on general positions of the unit cell (Fig. 8). The structure of **3** resembles the structure of **2**, however unlike to the chess-like ordering in **2**, in **3** one can distinguish cationic and anionic layers, alternating along the *b* axis (Fig. 9). The ET cations in the layers form pairs bonded by an inversion center. The anion layers are situated between the cation layers. In the anion layer, the metallacarboranes form herring-bone network (Fig. 9). The radical cations in the pairs are fully eclipsed (Fig. 10). The distances between averaged planes

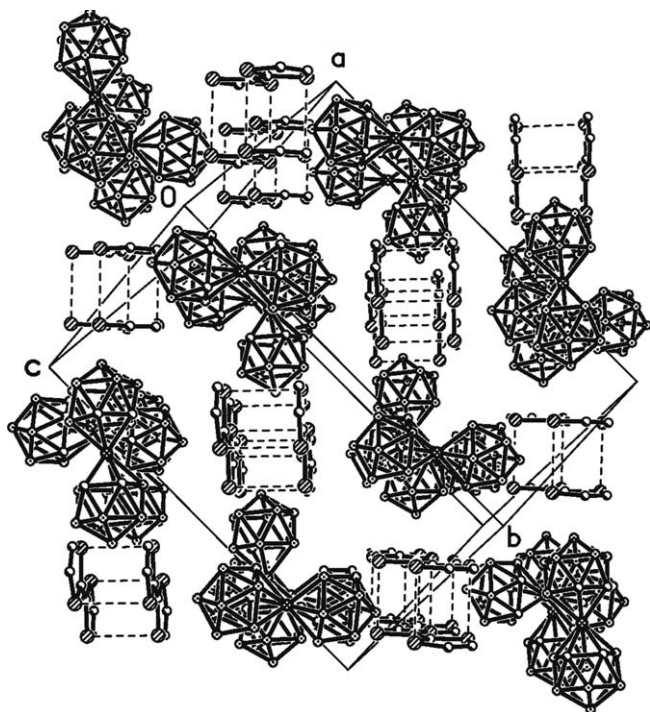


Fig. 6. A fragment of crystal structure of (TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

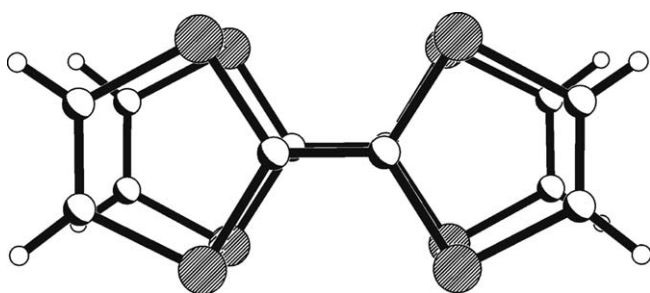


Fig. 7. Overlapping of TTF radical cations in the pair in the crystal structure of (TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

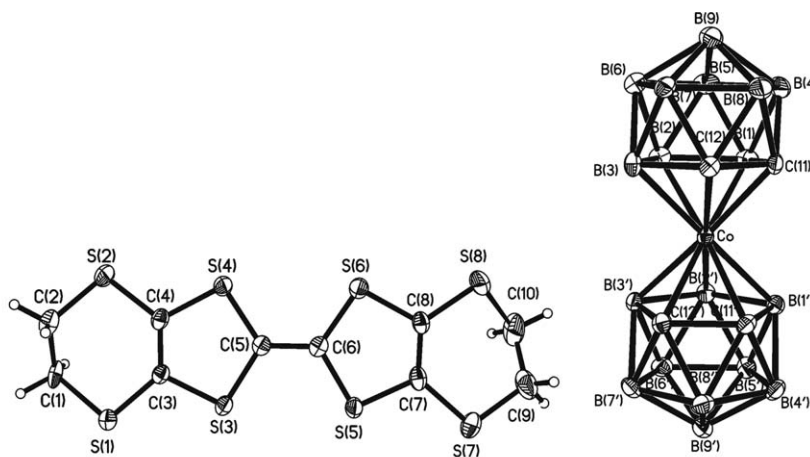


Fig. 8. Atomic designations in (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

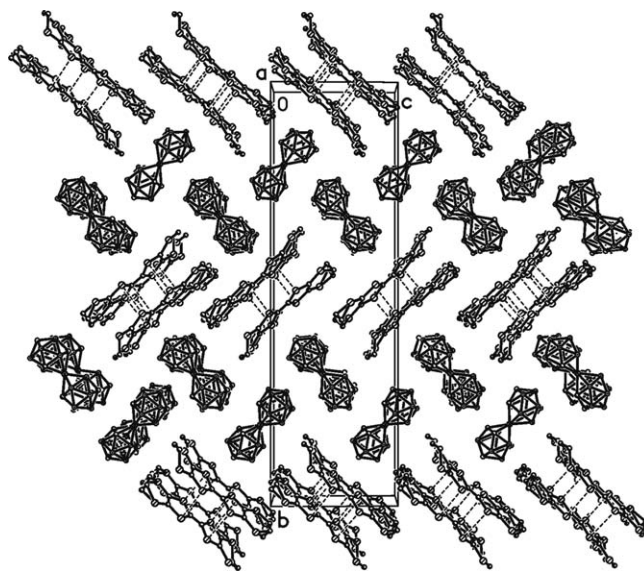


Fig. 9. A fragment of crystal structure of (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

of the radical cations in the pairs are 3.63 Å, the dihedral angle between the planes on symmetry conditions is 0°. The shortened S(3)⋯S(6) and S(4)⋯S(5) distances (3.40(4) Å and 3.45(4) Å, respectively) were found between the ET cations in the pairs (sum of van-der-Waals radii is 3.68 Å [18]). No intermolecular interaction between the pairs was found. The ET cations are bent, the maximum deviation of sulfur atoms from the cation plane being 0.15 Å and deviations of the carbon atoms of the ethylene groups amounting to 1.07 Å (C(10) atom).

The dicarbollide ligands in the [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ anion are mutually rotated by 36° producing *cisoid* conformation similar to that found in the structure 2. The C₂B₃ faces of the ligands nearly parallel (dihedral angle 3.5°). The distances from the cobalt atom to the C₂B₃ planes are equal 1.47 Å, and the metal is approximately equidistant from the facial boron and carbon atoms although

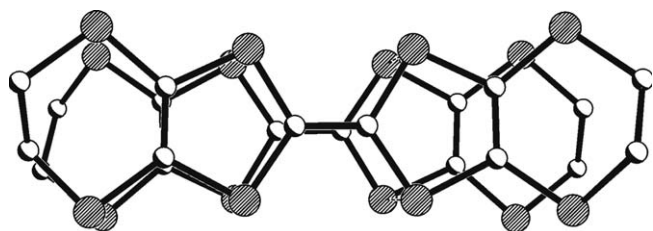


Fig. 10. Overlapping of ET radical cations in the stack in the crystal structure of (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

the Co–C distances are slightly shorter than the Co–B ones (mean values 2.045 and 2.095 Å, respectively) (Fig. 11).

2.4. Electrical conductivity and crystal structure peculiarities

The electrical conductivity study of the fulvalenium salts demonstrated that all they are semiconductors. The activation energy of **1**, E_a , was found to be 0.03 eV (Fig. 12). The room temperature conductivity is 15 Ohm⁻¹ cm⁻¹ that is the maximum value of conductivity for known metallacarborane radical cation salts. The room temperature conductivity of **2** is 10⁻⁸ Ohm⁻¹ cm⁻¹ that is in good agreement with the crystal structure of the compound (the absence of conducting layers or stacks). The activation energy of **3** equals $E_a \approx 0.18$ eV. The room temperature conductivity is 5 × 10⁻⁴ Ohm⁻¹ cm⁻¹. The temperature dependence of resistance for single crystal of **3** is shown in Fig. 13.

The results obtained demonstrate diversity of the crystal structure motifs and electric properties of the fulvalenium salts. On perfunctory inspection it can be explained by the difference in the radical cation size. However, the effect of metallacarborane counter ion has also great impact. Analysis of crystal packing in metallacarboranes (TTF)[3,3'-M(1,2-C₂B₉H₁₁)₂] (M = Co (**2**), Fe (**4**) [2], Ni (**5**) [2], Cr

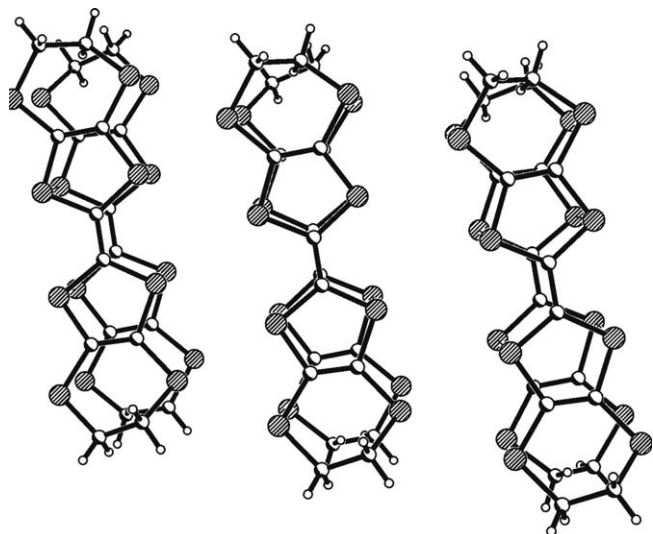


Fig. 11. ET rows in **B** (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

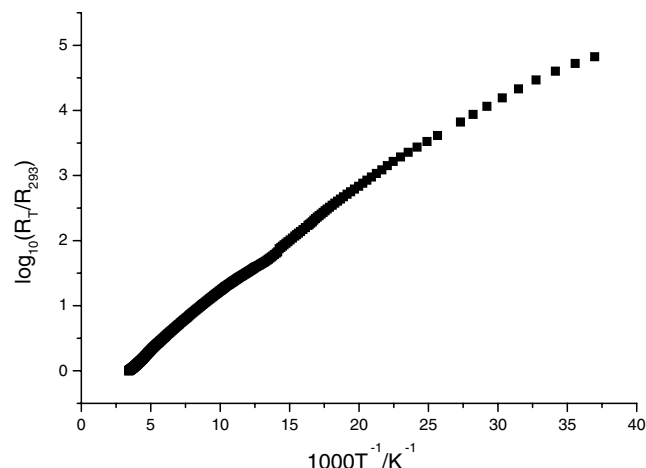


Fig. 12. The temperature dependence of resistance for the single crystal of (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂].

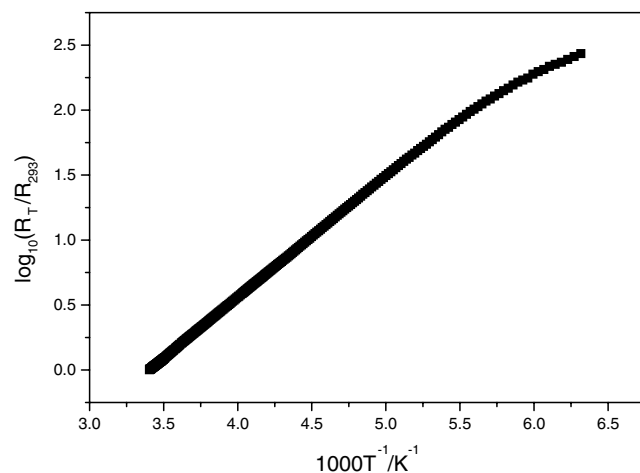


Fig. 13. The temperature dependence of resistance for the single crystal of (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂].

(**6**) [2] revealed that only the last compound has layered structure, whereas other ones contain discrete stacked dimers of the TTF radical cations and their crystals are isomorphous. Geometric parameters of the cation and anion parts in all these compounds are practically the same. What is the reason of the difference in the crystal packing? To answer this question we should consider conformation of the dicarbollide ligands in the metallacarborane anions. It was found, that in **6** the dicarbollide ligands adopt *transoid* conformation, whereas in **2**, **4**, and **5** they are in *cisoid* arrangement. The presence of two adjacent CH vertices in the bonding face of the dicarbollide ligand introduces localized regions of reduced negative charge and an antipodal concentration of negative charge. The asymmetry in the dicarbollide ligand charge distribution 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 is reasonably to suppose that crystals

comprising bis(dicarbollide) anions in *transoid* and *cisoid* arrangement, having very different dipole moments, should have different packing of these ions and, hence, different packing of counter ions. That is the case of metallacarboranes (TTF)[3,3'-M(1,2-C₂B₉H₁₁)₂].

The conformation of the dicarbollide ligands in bis(dicarbollide) complexes depend on nature and charge of the metal and, in principle, can be controlled by simple electron transfer processes or by photoexcitation [20].

The majority of reported X-ray structures of the cobalt bis(dicarbollide) anion [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ are either disordered or have *cisoid* arrangement of the ligands [5,21–24]. Two cobalt bis(dicarbollide) anions in different, *cisoid* and *transoid*, conformations were reported in structure of [Mn^{II}(1,10-Phen)₃][3,3'-Co^{III}(1,2-C₂B₉H₁₁)₂]₂ [25], however, in this case an alternative description of this compound as manganese(III) complex containing both cobalt(III) and cobalt(II) bis(dicarbollide) anions (the last one is in *transoid* conformation), [Mn^{III}(1,10-Phen)₃][3,3'-Co^{III}(1,2-C₂B₉H₁₁)₂][3,3'-Co^{II}(1,2-C₂B₉H₁₁)₂], cannot be ruled out. *Cisoid* conformation of both cobalt(III) bis(dicarbollide) ligands was found in the similar copper(II) complex [Cu^{II}(1,10-Phen)₃][3,3'-Co^{III}(1,2-C₂B₉H₁₁)₂]₂ [26].

It should be noted that the layered structure of compound **1** contains *transoid* conformation of the cobalt bis(dicarbollide) anion. This fact can be explained by two different ways. The first one is cathodic reduction of cobalt(III) to cobalt(II) bis(dicarbollide) under conditions of the electrochemical synthesis [27–32]. The second one is that the anion is sufficiently flexible to fine-tune its conformation to suit the arrangement found in the crystal structure. Rotation of the dicarbollide ligands in the cobalt bis(dicar-

bollide) anion [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ with respect to each other was shown to be rather facile, as judged by the low barriers for the conformer interconversion (less than 37 kJ mol⁻¹) [33], hence this possibility cannot be ruled out.

The stoichiometry of compound **1** is consistent both with (TMTSF^{0.5+})₂[3,3'-Co^{III}(1,2-C₂B₉H₁₁)₂]⁻ and (TMTSF⁺)₂[3,3'-Co^{II}(1,2-C₂B₉H₁₁)₂]²⁻ formulations. It was demonstrated earlier for the TTF salts that a lengthening of the bridging C=C bond and shortening of the C-S bonds involving the bridgehead carbons generally indicate an increase in positive charge on the TTF unit [34]. The same tendency was expected for TMTSF salts on the base of quantum-chemical calculations [35]. In order to determine charge of the TMTSF radical cation we examined bond lengths in a series of TMTSF salts of different stoichiometry [36–41]. Unfortunately, no such relationship between the bridging C=C bond length and the TMTSF charge was revealed. It should be noted that the relatively high conductivity of compound **1** is rather indicative of partial cationic oxidation with cobalt(III) anions than the full oxidation of the cations with the cobalt(II) anions (we are grateful to one of the referees for this suggestion), however, the question regarding the charge distribution in compound **1** still remains open.

Compound **3** differs from earlier reported (ET)₂[3,3'-Cr(1,2-C₂B₉H₁₁)₂] [4] both in composition and in crystal structure (the last compound has layered structure with metallacarborane anion in *transoid* conformation). Meanwhile their conductivities differ just by an order of magnitude (2 × 10⁻³ Ohm⁻¹ cm⁻¹ for (ET)₂[3,3'-Cr(1,2-C₂B₉H₁₁)₂]).

Table 1
Crystal data and structure refinement for (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**2**) and (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**)

Compound	1	2	3
Empiric formula	C ₂₄ H ₄₆ B ₁₈ CoSe ₈	C ₁₀ H ₂₆ B ₁₈ CoS ₄	C ₁₄ H ₃₀ B ₁₈ CoS ₈
Formula weight	1219.80	528.06	708.37
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1 (No. 1)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	7.572(5)	11.228(2)	6.774(1)
<i>b</i> (Å)	12.146(8)	20.290(3)	38.381(6)
<i>c</i> (Å)	13.008(8)	11.745(2)	11.524(3)
α (°)	116.20(3)	90	90
β (°)	93.18(3)	115.00(2)	91.96(2)
γ (°)	102.52(3)	90	90
<i>V</i> (Å ³)	1032.2(1)	2425.0(7)	2994.4(1)
<i>Z</i>	1	4	4
λ (Å)	0.71073	0.71073	0.71073
<i>D</i> _{calc} (Mg m ⁻³)	1.96	1.45	1.57
μ (mm ⁻¹)	7.490	1.054	1.144
Number of reflections collected	4379	3273	4195
Number of independent reflections	4379	3102	3817
Number of reflections with [<i>F</i> ₀ > 4σ(<i>F</i> ₀)]	2501	2305	2918
Number of parameters refined	233	403	399
(2θ) _{max} (°)	53.94	44.92	44.96
<i>R</i>	0.069	0.032	0.037

3. Conclusion

New radical cation salts (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**), (TTF)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**2**) and (ET)[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**3**) were synthesized and their crystal structures and electrical conductivities were determined. Compound **1** has structure with regular conducting stacks of the TMTSF cations, whereas compounds **2** and **3** contain separated pairs of fulvalenium cations. Conductivity of crystals **1** at room temperature was found to be 15 Ohm⁻¹ cm⁻¹, that is the maximum value for fulvalenium metallacarborane salts.

4. Experimental

4.1. Synthesis

Na[3,3'-Co(1,2-C₂B₉H₁₁)₂] was prepared by the literature method [27]. [D][3,3'-Co(1,2-C₂B₉H₁₁)₂] crystals,

Table 2
Selected bond distances and bond angles for (TMTSF)₂[3,3'-Co(1,2-C₂B₉H₁₁)₂] (**1**)

TMTSF radical cation			
Bond length	<i>d</i> (Å)		
C(5)–C(6)	1.35(1)	Se(4)–C(8)	1.906(8)
C(5)–Se(1)	1.885(7)	C(3)–C(4)	1.37(1)
C(5)–Se(2)	1.863(8)	C(7)–C(8)	1.35(1)
C(6)–Se(3)	1.881(7)	C(1)–C(3)	1.51(1)
C(6)–Se(4)	1.885(8)	C(2)–C(4)	1.53(1)
Se(1)–C(3)	1.895(8)	C(7)–C(9)	1.51(1)
Se(2)–C(4)	1.869(9)	C(8)–C(10)	1.49(1)
Se(3)–C(7)	1.890(9)		
Bond angle	ω (°)		
Se(1)–C(5)–Se(2)	114.5(4)	Se(2)–C(4)–C(3)	120.6(7)
Se(3)–C(6)–Se(4)	113.5(4)	Se(3)–C(7)–C(8)	119.8(7)
Se(1)–C(5)–C(6)	122.4(6)	Se(4)–C(8)–C(7)	116.8(6)
Se(2)–C(5)–C(6)	123.1(6)	Se(1)–C(3)–C(1)	117.7(6)
Se(3)–C(6)–C(5)	123.8(6)	Se(2)–C(4)–C(2)	115.7(6)
Se(4)–C(6)–C(5)	122.7(6)	Se(3)–C(7)–C(9)	114.8(6)
C(3)–Se(1)–C(5)	94.8(3)	Se(4)–C(8)–C(10)	116.0(6)
C(4)–Se(2)–C(5)	94.1(3)	C(1)–C(3)–C(4)	126.5(8)
C(6)–Se(3)–C(7)	94.5(3)	C(2)–C(4)–C(3)	123.7(8)
C(6)–Se(4)–C(8)	95.4(3)	C(8)–C(7)–C(9)	125.3(9)
Se(1)–C(3)–C(4)	116.0(6)	C(7)–C(8)–C(10)	127.2(8)
[3,3'-Co(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻ anion			
Bond length	<i>d</i> (Å)		
Co–C(11)	2.041(8)	B(3)–B(7)	1.75(1)
Co–C(12)	2.019(8)	B(1)–B(5)	1.79(1)
Co–B(1)	2.119(9)	B(3)–B(6)	1.76(1)
Co–B(3)	2.070(8)	B(2)–B(5)	1.80(1)
Co–B(2)	2.110(9)	B(2)–B(6)	1.79(1)
C(11)–C(12)	1.65(1)	B(4)–B(8)	1.77(1)
C(11)–B(1)	1.75(1)	B(7)–B(8)	1.77(1)
C(12)–B(3)	1.71(1)	B(4)–B(5)	1.76(1)
B(1)–B(2)	1.78(1)	B(6)–B(7)	1.79(1)
B(2)–B(3)	1.74(1)	B(5)–B(6)	1.77(1)
C(11)–B(8)	1.76(1)	B(8)–B(9)	1.76(1)
C(12)–B(8)	1.76(1)	B(4)–B(9)	1.78(1)
C(11)–B(4)	1.73(1)	B(7)–B(9)	1.79(1)
C(12)–B(7)	1.71(1)	B(5)–B(9)	1.75(1)
B(1)–B(4)	1.78(1)	B(6)–B(9)	1.78(1)

where D – TTF, ET or TMTSF were prepared by anodic oxidation of D π -donor on platinum electrodes under galvanostatic conditions. The fulvalene concentrations were about 2×10^{-3} mol/l and Na[3,3'-Co(1,2-C₂B₉H₁₁)₂] electrolyte concentration was 1×10^{-2} mol/l. The crystals of optimal quality were obtained from mixed solvents: 1,1,2-trichloroethane–acetonitrile or chloromethylene–acetonitrile (20:1), $I = 0.20 \pm 0.50$ μ A. The syntheses time was 3–4 weeks. In each case shining black needle-shaped crystals were obtained.

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

TTF radical cation			
Bond length	<i>d</i> (Å)		
C(3)–C(4)	1.390(4)	S(2)–C(2)	1.715(4)
C(3)–S(1)	1.716(3)	S(3)–C(5)	1.727(4)
C(3)–S(2)	1.710(3)	S(4)–C(6)	1.717(4)
C(4)–S(3)	1.719(3)	C(1)–C(2)	1.311(5)
C(4)–S(4)	1.722(3)	C(5)–C(6)	1.300(6)
S(1)–C(1)	1.716(4)		
Bond angle	ω (°)		
S(1)–C(3)–S(2)	115.4(2)	C(2)–S(2)–C(3)	95.06(2)
S(3)–C(4)–S(4)	115.1(2)	C(4)–S(3)–C(5)	94.5(2)
S(1)–C(3)–C(4)	122.8(2)	C(4)–S(4)–C(6)	94.8(2)
S(2)–C(3)–C(4)	121.9(2)	S(1)–C(1)–C(2)	117.8(3)
S(3)–C(4)–C(3)	123.0(3)	S(2)–C(2)–C(1)	117.2(3)
S(4)–C(4)–C(3)	121.8(2)	S(3)–C(5)–C(6)	117.8(3)
C(1)–S(1)–C(3)	94.59(2)	S(4)–C(6)–C(5)	117.7(4)
[3,3'-Co(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻ anion			
Bond length	<i>d</i> (Å)		
Co–C(11)	2.040(3)	B(3)–B(7)	1.771(6)
Co–C(11')	2.050(3)	B(3')–B(7')	1.795(5)
Co–C(12)	2.044(3)	B(1)–B(5)	1.774(6)
Co–C(12')	2.044(3)	B(1')–B(5')	1.774(6)
Co–B(1)	2.089(4)	B(3)–B(6)	1.739(6)
Co–B(1')	2.092(4)	B(3')–B(6')	1.771(6)
Co–B(3)	2.077(4)	B(2)–B(5)	1.781(6)
Co–B(3')	2.081(4)	B(2')–B(5')	1.795(6)
Co–B(2)	2.106(4)	B(2)–B(6)	1.797(6)
Co–B(2')	2.091(4)	B(2')–B(6')	1.794(5)
C(11)–C(12)	1.624(4)	B(4)–B(8)	1.757(5)
C(11')–C(12')	1.607(4)	B(4')–B(8')	1.764(6)
C(11)–B(1)	1.722(5)	B(7)–B(8)	1.762(6)
C(11')–B(1')	1.688(5)	B(7')–B(8')	1.757(5)
C(12)–B(3)	1.665(5)	B(4)–B(5)	1.771(6)
C(12')–B(3')	1.692(4)	B(4')–B(5')	1.761(5)
B(1)–B(2)	1.777(6)	B(6)–B(7)	1.758(5)
B(1')–B(2')	1.792(5)	B(6')–B(7')	1.769(5)
B(2)–B(3)	1.787(5)	B(5)–B(6)	1.778(6)
B(2')–B(3')	1.795(5)	B(5')–B(6')	1.784(6)
C(11)–B(8)	1.731(5)	B(8)–B(9)	1.765(5)
C(11')–B(8')	1.715(5)	B(8')–B(9')	1.762(5)
C(12)–B(8)	1.707(5)	B(4)–B(9)	1.775(6)
C(12')–B(8')	1.715(5)	B(4')–B(9')	1.774(6)
C(11)–B(4)	1.698(5)	B(7)–B(9)	1.779(6)
C(11')–B(4')	1.691(5)	B(7')–B(9')	1.774(6)
C(12)–B(7)	1.695(5)	B(5)–B(9)	1.776(5)
C(12')–B(7')	1.684(5)	B(5')–B(9')	1.791(6)
B(1)–B(4)	1.795(5)	B(6)–B(9)	1.797(6)
B(1')–B(4')	1.783(5)	B(6')–B(9')	1.781(5)

4.2. Electroconductivity measurements

The electrical resistance of the crystals was measured by the standard dc-four-probe method at direct current in the interval of 100–295 K.

4.3. X-ray diffraction analysis

X-ray diffraction studies were carried out with an Enraf Nonius CAD-4 diffractometer, using graphite monochro-

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

ET radical cation			
Bond length	<i>d</i> (Å)		
C(5)–C(6)	1.39(8)	C(3)–S(1)	1.74(6)
C(5)–S(3)	1.73(6)	C(4)–S(2)	1.75(6)
C(5)–S(4)	1.72(6)	C(7)–C(7)	1.74(6)
C(6)–S(5)	1.71(6)	C(8)–S(8)	1.75(6)
C(6)–S(6)	1.71(6)	S(1)–C(1)	1.80(8)
S(3)–C(3)	1.73(5)	S(2)–C(2)	1.78(8)
S(4)–C(4)	1.75(6)	S(7)–C(9)	1.76(7)
S(5)–C(7)	1.72(6)	S(8)–C(10)	1.78(3)
S(6)–C(8)	1.73(6)	C(1)–C(2)	1.53(12)
C(3)–C(4)	1.34(8)	C(9)–C(10)	1.49(6)
C(7)–C(8)	1.35(8)		
Bond angle	ω (°)		
S(3)–C(5)–S(4)	115(3)	S(2)–C(4)–S(4)	115(3)
S(5)–C(6)–S(6)	115(3)	S(2)–C(7)–S(7)	114(3)
S(3)–C(5)–C(6)	121(4)	S(6)–C(8)–S(8)	118(3)
S(4)–C(5)–C(6)	124(4)	S(1)–C(3)–C(4)	130(4)
S(5)–C(6)–C(5)	124(4)	S(2)–C(4)–C(3)	128(4)
S(6)–C(5)–C(6)	121(4)	S(7)–C(7)–C(8)	129(5)
C(3)–S(3)–C(5)	96(3)	S(8)–C(8)–C(7)	126(5)
C(4)–S(4)–C(5)	96(3)	C(1)–S(1)–C(3)	101(3)
C(6)–S(5)–C(7)	96(3)	C(2)–S(2)–C(4)	99(3)
C(6)–S(6)–C(8)	96(3)	C(7)–S(7)–C(9)	105(3)
S(3)–C(3)–C(4)	117(4)	C(8)–S(8)–C(10)	99(2)
S(4)–C(4)–C(3)	117(4)	S(1)–C(1)–C(2)	112(6)
S(5)–C(7)–C(8)	117(5)	S(2)–C(2)–C(1)	114(6)
S(6)–C(8)–C(7)	116(4)	S(7)–C(9)–C(10)	118(5)
S(1)–C(3)–S(3)	114(3)	S(8)–C(10)–C(9)	117(3)
[3,3'-Co(1,2-C ₂ B ₉ H ₁₁) ₂] ⁻ anion			
Bond length	<i>d</i> (Å)		
Co–C(11)	2.03(2)	C(12)–B(7)	1.68(7)
Co–C(11')	2.05(2)	B(1)–B(4)	1.79(9)
Co–C(12)	2.05(2)	B(3)–B(7)	1.79(9)
Co–C(12')	2.05(2)	B(1)–B(5)	1.77(9)
Co–B(1)	2.08(7)	B(3)–B(6)	1.77(9)
Co–B(1')	2.09(6)	B(2)–B(5)	1.79(9)
Co–B(3)	2.10(6)	B(2)–B(6)	1.80(9)
Co–B(3')	2.07(6)	B(4)–B(8)	1.76(9)
Co–B(2)	2.12(6)	B(7)–B(8)	1.75(9)
Co–B(2')	2.11(6)	B(4)–B(5)	1.75(10)
C(11)–C(12)	1.61(8)	B(6)–B(7)	1.78(9)
C(11)–B(1)	1.70(7)	B(5)–B(6)	1.77(9)
C(12)–B(3)	1.70(6)	B(8)–B(9)	1.74(10)
B(1)–B(2)	1.80(9)	B(4)–B(9)	1.76(9)
B(2)–B(3)	1.80(8)	B(7)–B(9)	1.75(9)
C(11)–B(8)	1.73(7)	B(5)–B(9)	1.77(9)
C(12)–B(8)	1.72(7)	B(6)–B(9)	1.78(9)
C(11)–B(4)	1.68(7)		

mated Mo K α radiation ($\omega/2\theta$ -scanning). The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 in anisotropic for non-hydrogen atoms approximation. The hydrogen atoms in **1** were placed in idealised positions, the hydrogen atoms in **2** were located from the difference Fourier syntheses and refined in isotropic approximation, whereas the hydrogen atoms in **3** were determined partially from the difference Fourier synthesis and partially calculated. The reflection intensities were corrected for absorption using semi-empirical method [42]. The analysis of Fourier density synthesis in **3** have revealed that C(1) and C(2) atoms of the ET cation-radical are disordered over two positions, which were refined with approximately equal occupancies. All calculations were performed using the SHELXTL software [43]. Details of the data collection, structure solution and refinement are listed in Table 1. Selected bond distances and angles are presented in Tables 2–4.

5. Supplementary material

The crystallographic data have been deposited to the Cambridge Crystallographic Data Centre (CCDC-294658, 294659, 294657, for **1**, **2**, and **3**, respectively). Copies of the data can be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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