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Synthesis and study of *C*-substituted methylthio derivatives of cobalt bis(dicarbollide)†

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The *C*-methylthio derivatives of cobalt bis(dicarbollide) were synthesized by reaction of anhydrous $CoCl_2$ with *nido*-carborane $[7\text{-MeS-}7,8\text{-}C_2B_9H_{11}]^-$ and isolated as a mixture of *rac*-$[1,1'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ and *meso*-$[1,2'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ isomers. The structures of both isomers were studied using DFT quantum chemical calculations. The most preferable geometry of rotamers and the stabilization energy of *C*-methylthio derivatives of cobalt bis(dicarbolide) were calculated. The (BEDT-TTF)$[1,1'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]$ salt was prepared and its structure was determined by single crystal X-ray diffraction. The cisoid conformation of the *rac*-$[1,1'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ anion is stabilized by short intramolecular CH⋯S hydrogen and BH⋯S chalcogen bonds between the dicarbollide ligands, that is in good agreement with the data of quantum chemical calculations.

Introduction

The synthesis of the first carboranes in the early 1960s, followed by the rapid development of their chemistry, resulted in the creation of a number of new carborane-based materials with unique properties.[1–5] Among the various derivatives of carboranes, special attention is paid to π-complexes of transition metals with carborane ligands, called metallacarboranes. The most known of them, cobalt bis(dicarbollide) $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ attracts increasing interest from researchers working in various fields from medical chemistry to[6–11] materials science[12–18] to due to its extraordinary high stability, low toxicity[19] and almost unlimited possibilities for chemical modification.[20,21]

Recently, we suggested that cobalt bis(dicarbollide) can be used as a structural element in the design of molecular switches.[22] Molecular switches are molecules or supramolecular complexes that can exist in two or more stable forms that differ in the mutual orientation of their components and can be converted readily from one state to another by various external stimuli such as heat, light, chemicals, *etc.*[23] Indeed, when studying a series of isomeric *B*-methylthio derivatives of cobalt bis(dicarbollide), we found that in the 8,8′-isomer $[8,8'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ stabilization of the transoid conformation is reached due to two pairs of intramolecular $CH_{carb}\cdots S$ hydrogen bonds between the ligands, whereas in the 4,4′-isomer $[4,4'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ two pairs of the $CH_{carb}\cdots S$ hydrogen bonds stabilize the *gauche* conformation. In the case of the 4,7′-isomer $[4,7'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$, due to steric reasons the *gauche* conformation is stabilized by only one pair of the $CH_{carb}\cdots S$ hydrogen bonds.[24] The addition of an external metal of labile metallacomplex to the 8,8′-isomer leads to the breaking weak hydrogen bonds and the appearance of stronger dative S→M bonds that accompanies by a change in conformation from transoid to cisoid one.[25] In this contribution we report the synthesis and study of *C*-methylthio derivatives of cobalt bis(dicarbollide).

Results and discussion

Synthesis of *C*-substituted methylthio derivatives of cobalt bis(dicarbollide)

To synthesize the *C*-methylthio derivatives of cobalt bis(dicarbollide) we used reaction of anhydrous $CoCl_2$ with 7-methylthio-*nido*-carborane $[7\text{-MeS-}7,8\text{-}C_2B_9H_{11}]^-$ (ref. 26) in 1,2-dimethoxyethane in the presence of potassium *tert*-butoxide (Scheme 1). The reaction results in a mixture of *rac*-$[1,1'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ and *meso*-$[1,2'\text{-(MeS)}_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ isomers in 1 : 1 molar ratio; all attempts to separate them by chromatographic methods have been unsuccessful.

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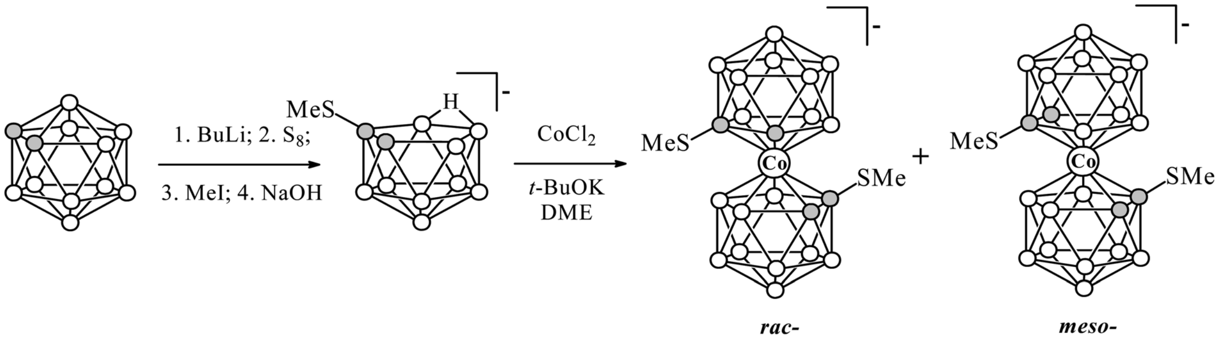

Scheme 1 Synthesis of *C*-substituted methylthio derivatives of cobalt bis(dicarbollide).

The *C*-methylthio derivatives of paramagnetic iron bis(dicarbollide) were prepared in a similar way (See ESI†). The formation of an equimolar mixture of the *rac*- and *meso*-isomers in the reactions with asymmetrically substituted *nido*-carboranes is quite expected and was observed earlier for $[9\text{-MeS-}7,8\text{-}C_2B_9H_{11}]^-$ (isomers were separated),[24] $[7\text{-EtS-}7,8\text{-}C_2B_9H_{10}]^-$ and $[7\text{-EtS-}8\text{-R-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Me, Ph) (isomers were not separated).[27,28] However, in some cases, *e.g.* in a similar reaction with $[9\text{-MeO-}7,8\text{-}C_2B_9H_{11}]^-$ only one isomer is formed,[29] that could be explained by lower stability of second isomer under synthesis and/or isolation conditions. It should be noted that all our attempts to synthesize cobalt and iron bis(dicarbollide) complexes based on 7,8-di(methylthio)-*nido*-carborane $[7,8\text{-}(MeS)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ failed.

The ^1H NMR spectrum of the reaction product contains characteristic signals of the carborane CH groups at 4.33, 4.29 and 4.00 ppm with an integral intensity ratio of 1 : 1 : 2, as well as two signals of the MeS groups at 2.40 (narrow) and 2.28 (wide) ppm with an integral intensity ratio of 3 : 3 (Fig. 1). The appearance of three signals of the carborane CH groups indicates a confined mutual rotation of dicarbollide ligands. Moreover, it is reasonable to assume that one of the isomers has two equivalent carborane CH groups, whereas in another one these groups are nonequivalent. This nonequivalence can be caused by the participation of the CH groups in the formation of intramolecular $CH_{carb}\cdots S$ hydrogen bonds between the ligands similar to found in the *B*-substituted methylthio derivatives.[24] In this case, in the *rac*-isomer $[1,1'\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ both CH groups can form intramolecular $CH_{carb}\cdots S$ hydrogen bonds, while in the *meso*-isomer $[1,2'\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ only one CH group can participate in such bonding for steric reasons. To verify this assumption, quantum chemical calculations were performed.

Quantum-chemical calculations of $[X,Y'\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ rotamers

Both for *rac*-$[1,1'\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ and *meso*-$[1,2'\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ isomers five rotamers were identified as minima on the PES, totally 10 isomers (Fig. 2,

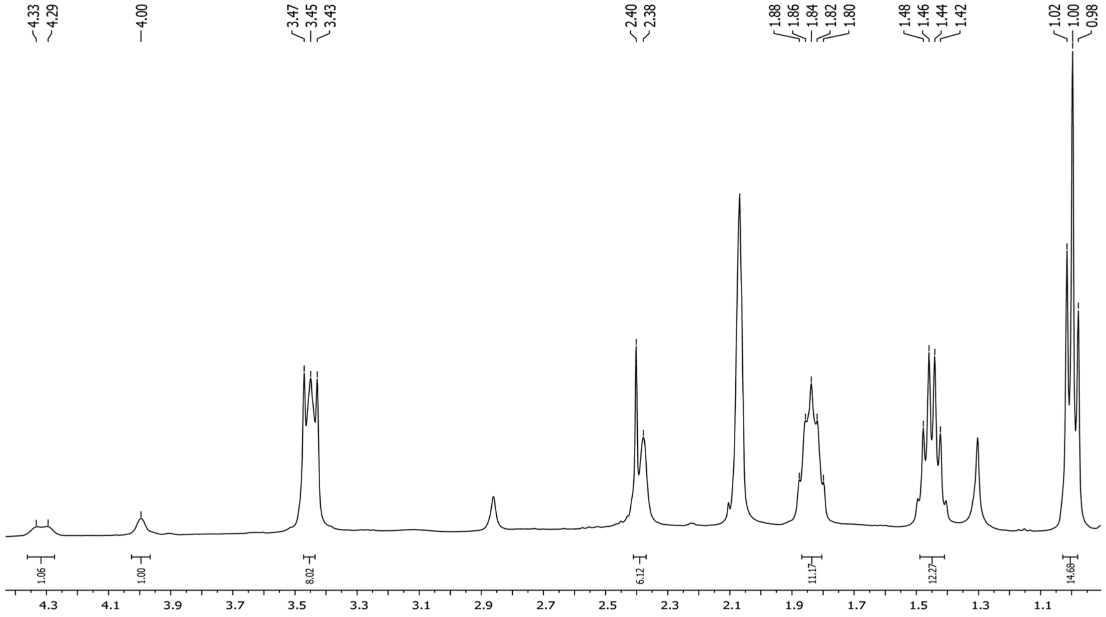

Fig. 1 ^1H NMR spectrum of $(Bu_4N)[1,1'(2')\text{-}(MeS)_2\text{-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]$ in acetone-d_6.

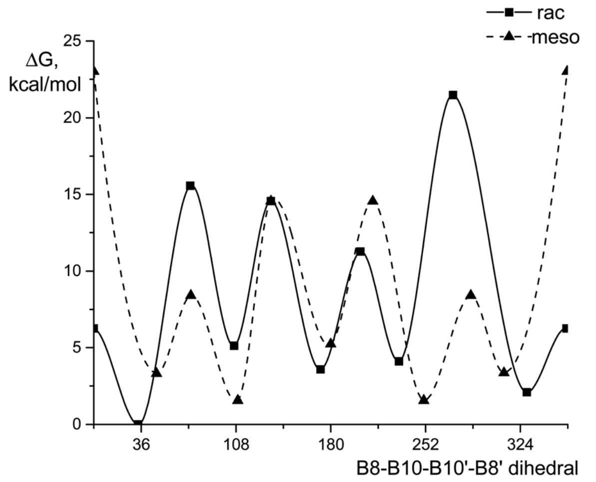

Fig. 2 The rotational profile of *rac*-$[1,1'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ and *meso*-$[1,2'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ isomers. ΔG^{298} values are related to the global minimum of cisoid conformation of the *rac*-isomer.

Table S1†). Due to symmetry of 1,2′-substituted cobalt bis(dicarbollide) (*meso*-isomer), the two possible cisoid- and *gauche*-rotamers are pairwise identical enantiomers. Therefore three conformers (transoid-, *gauche*- and cisoid-) will be discussed for *meso*-$[1,2'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ and five (single *trans*-, two *gauche*- and two cisoid-) for *rac*-$[1,1'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ (Fig. 3) hereinafter.

Despite geometry optimizations were performed without symmetry restrictions the all five rotamers of *rac*-isomer are close to the C_2 symmetry, while only transoid-rotamer of the *meso*- has a symmetry point group (C_i). For the *rac*-isomer, the global minimum among all possible rotamers corresponds to the cisoid1 conformation stabilized by two CH⋯S and two BH⋯S interactions between the dicarbollide ligands (Fig. 3). It is noteworthy that this global minimum corresponds exactly to the rotamer that was found in the X-ray structure of the BEDT-TTF salt (see below, Table S2†). The same conformation was found earlier in the X-ray structure of $\{(Me_2CO)_2Na[rac\text{-}1,1'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{10})_2]\}$.[30] The second most preferred rotamer is a cisoid2-, which is 2.1 kcal mol^{-1} higher, while *gauche*1-, *gauche*2- and transoid-rotamers are 5.1, 3.6 and 4.1 kcal mol^{-1} higher, than the cisoid1-rotamer on the ΔG^{298} scale. The cisoid2- and *gauche*2- rotamers features S⋯S interaction and as the consequence the rotational barrier between them requiring the movement of sulfur atoms close to each other is the highest on the rotational PES. Additionally, the cisoid2-rotamer is stabilized by two CH⋯S interactions, while the *gauche*2-rotamer has two BH⋯S interactions. In a turn, the transoid- and *gauche*2-rotamers possess four BH⋯S bond critical points (BCP's) each. Energy of these interactions with S atom E_{BCP} are in -(1.6–2.3) kcal mol^{-1} range with their sum being 6.2–7.9 kcal mol^{-1}.

The most favorable for the *meso*-$[1,2'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ isomer *gauche*-rotamer is stabilized by three BH⋯S and one CH⋯S interactions (E_{BCP} are in −(1.4–2.3) kcal mol^{-1} range, with their sum being 7.5 kcal mol^{-1}). The corresponding cisoid conformer is stabilized by one BH⋯S and one CH⋯S interactions as well as by S⋯S interaction and is only 1.7 kcal mol^{-1} less preferable, than the *gauche*-rotamer. The barrier between two equivalent cisoid-rotamers featuring S⋯S interactions is highest on the rotational PES. It is worth noting that namely the cisoid-rotamer was found earlier in the X-ray structure of $\{(Me_2CO)Na[meso\text{-}1,2'\text{-}\mu\text{-}\{S(CH_2CH_2O)_3CH_2CH_2S\}\text{-}3,3'\text{-}Co\text{-}(1,2\text{-}C_2B_9H_{10})_2]\}\cdot 2CHCl_3$, where mutual rotation of the dicarbollide ligands is additionally restricted by the complexation of the sodium cation with the oligoethyleneglycol bridge connecting both dicarbollide ligands.[30] The transoid-rotamer slightly is stabilized by four BH⋯S interactions but is the least favorable ($\Delta G^{298} = 3.6$ kcal mol^{-1}).

It should be noted that the CH groups in the cisoid-conformation of the *rac*-isomer are equivalent, bonded to the S(Me) group of the second dicarbollide ligand ($r(\text{CH}\cdots\text{S}) = 2.693$ Å, $E_{BCP} = 2.1$ kcal mol^{-1}), whereas the *guache*-conformation of the *meso*-isomer has non-equivalent CH groups, one being bonded with S atom (2.797 Å, $E_{BCP} = 1.7$ kcal mol^{-1}), while second in not connected by the bond path to any neighbor. This rationalizes the ^{1}H NMR spectrum where two resonances of CH groups were observed.

The DFT analysis of PES of mutual rotation of the dicarbollide ligands predicts free rotation at room temperature (the second highest barrier is $\Delta G^{\#} = 15.6$ and 13.0 kcal mol^{-1} for *rac*- and *meso*-isomers, respectively). The highest rotational transition states on the PES are by 21.5 kcal mol^{-1} higher than the lowest energy rotamer, but their passing is not required for formation of every possible isomer. The second favorable rotamer located 2.1 kcal mol^{-1} above the most favored one for the *rac*-isomer and 1.7 kcal mol^{-1} for the *meso*-isomer, suggesting their possible presence in solution at amounts <5%. Therefore observation of only one – the most favorable rotamer for each isomer is well rationalized by the DFT calculations.

Synthesis, structure and properties of (BEDT-TTF)$[1,1'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]$

In a systematic study of the tetrathiafulvalene salts of transition metal bis(dicarbollides), we found that various substituents in the dicarbollide ligands have a great influence on their crystal structure and electroconductive properties.[13,31] In addition to the stabilization of certain rotamers of bis(dicarbollide) complexes due to intramolecular hydrogen bonding, *exo*-polyhedral substituents also can participate in intermolecular bonding with other anions and the tetrathiafulvalene radical-cations.[32–36] This prompted us to synthesize similar compounds with methylthio derivatives of cobalt bis(dicarbollide). It should be noted that our initial attempt to obtain the BEDT-TTF salt with the with $[8,8'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ anion was unsuccessful due to the ease of oxidation of sulfur atoms,[24] which, probably, can be explained by the strong electron-donating effect of the cobaltacarborane cage bound *via* boron atom. On the other hand, in the case of the MeS group attached to the carbon atom, the electron-withdrawing nature of the cobaltacarborane cage should result in an increase of the oxidative stability of the substituent.[37]

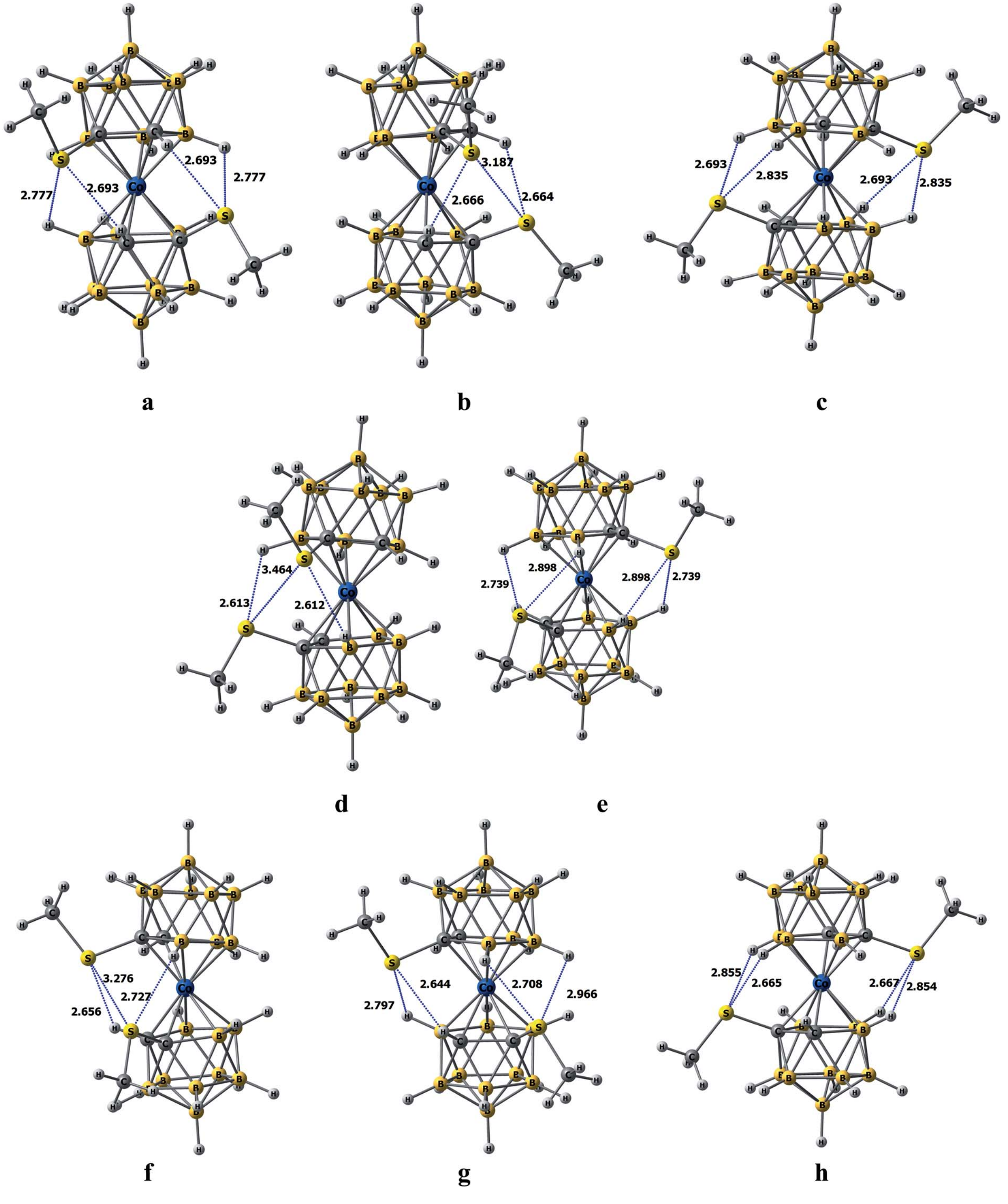

Fig. 3 Structures of rotamers for *rac*-$[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (a – cisoid1, b – cisoid2, c – *gauche*1, d – *gauche*2, e – transoid) and *meso*-$[1,2'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (f – cisoid, g – *gauche*, h – transoid) isomers.

Indeed, we were able to obtain single crystals of the salt of the 1 : 1 radical-cation salt (BEDT-TTF)$[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ electrochemically by anodic oxidation of BEDT-TTF in the presence of $(Me_4N)[1,1'(2')-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ in a mixture of 1,1,2-trichloroethane–acetonitrile (12 : 1) as a solvent. It is noteworthy that the electrocrystallization leads to selective isolation of only one isomer, namely the *rac*-isomer. The crystal structure is formed by the BEDT-TTF radical-cation in a general position and enantiomeric anions $[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**A**) and $[2,2'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (**B**) in special positions on a two-fold axis of the unit cell (Fig. 4). The dicarbollide ligands in the anions are mutually rotated by 33.2 and 35.1°, for **A** and **B** respectively, adopting cisoid conformation. The cisoid conformation is stabilized by short

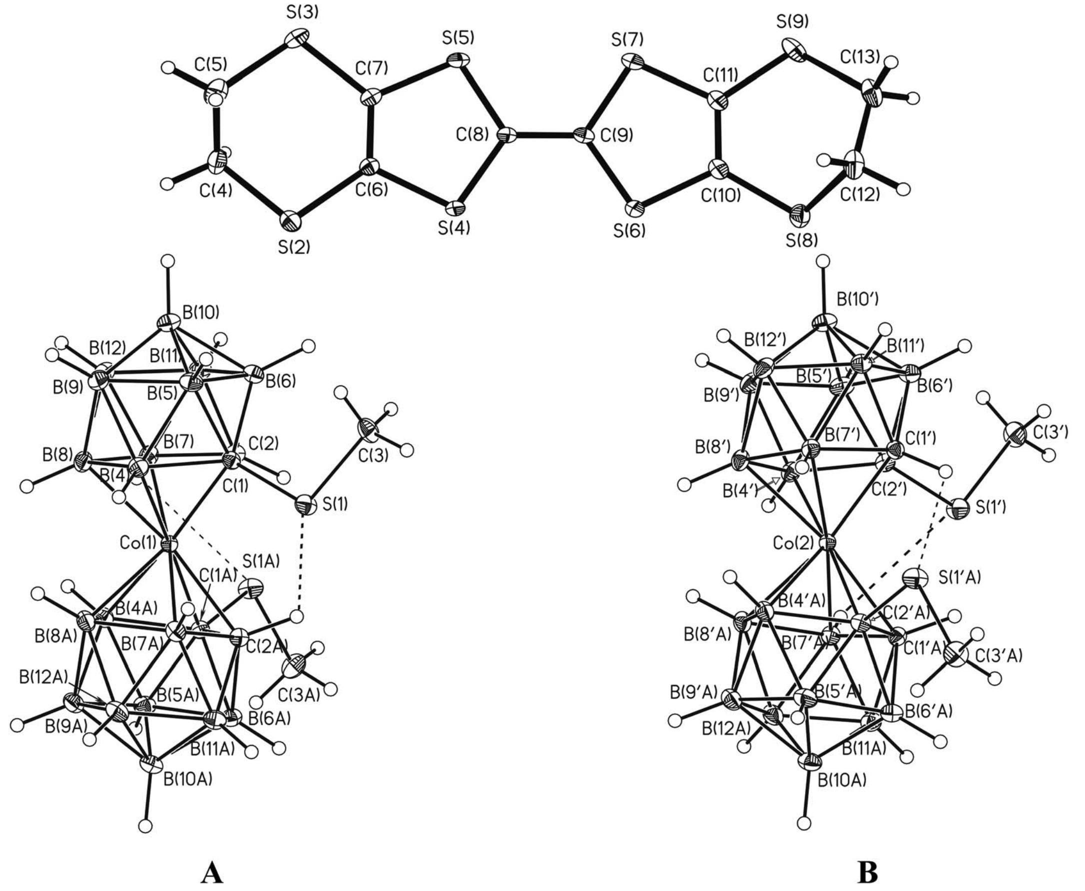

Fig. 4 BEDT-TTF radical-cations and $[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (A) and $[2,2'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]^-$ (B) anions. Dashed lines show intramolecular CH···S and BH···S contacts.

intramolecular C(2)H···S(1) hydrogen (2.561 and 2.603 Å for **A** and **B**, respectively) and B(7)H···S(1) chalcogen (2.843 and 2.837 Å for **A** and **B**, respectively) bonds, that is in good agreement with the data of quantum chemical calculations. Similar CH···S (2.513 and 2.579 Å) and BH···S (2.901 and 3.009 Å) bonds were found earlier in X-ray structure of $\{(Me_2CO)_2Na[$*rac*-1,1′-μ-$\{S(CH_2CH_2O)_3CH_2CH_2S\}$-3,3′-Co-$(1,2-C_2B_9H_{10})_2]\}$, however in that case mutual ligand rotation is additionally restricted by the complexation of the sodium cation with the oligoethyleneglycol bridge connecting both dicarbollide ligands.[30] It should be noted that the cobalt bis(dicarbollide) anions are characterized by a rather distorted geometry: the C_2B_3 planes of the dicarbollide ligands form a dihedral angle of 170.8° for anion A and 170.5° for anion **B**.

The formation of chalcogen bonds is generally explained in terms of the positive electrostatic potential present on the outermost portion of the chalcogen's surface, so-called "σ-hole". This "σ-hole" can interact attractively with negative sites of the same molecule or other molecules.[38,39] The acceptors of the chalcogen bond usually are atoms having an unshared electron pair, π-systems or halide anions. To the best of our knowledge, there are only a few examples of the formation of chalcogen bonds with boron hydrides as acceptors and all them were found in the MeS derivatives of transition metal bis(dicarbollide) complexes.[24,40,41]

In the crystal structure, the pairs of **A** and **B** enantiomers alternate with the BEDT-TTF radical-cation dimers. In the dimers, the radical-cations are bound by shortened S···S

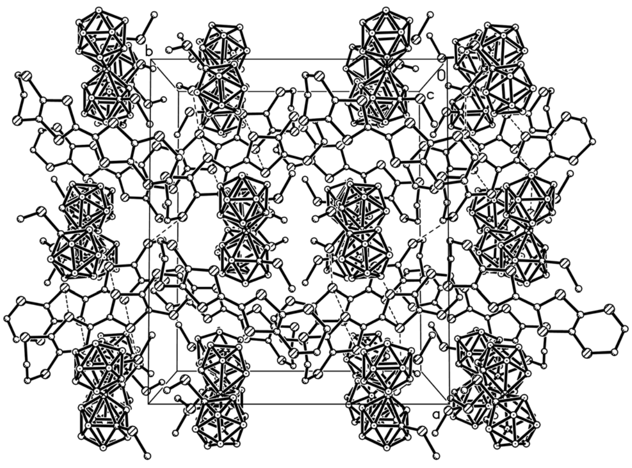

Fig. 5 Crystal packing in the structure of (BEDT-TTF)$[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ (hydrogen atoms are omitted for clarity).

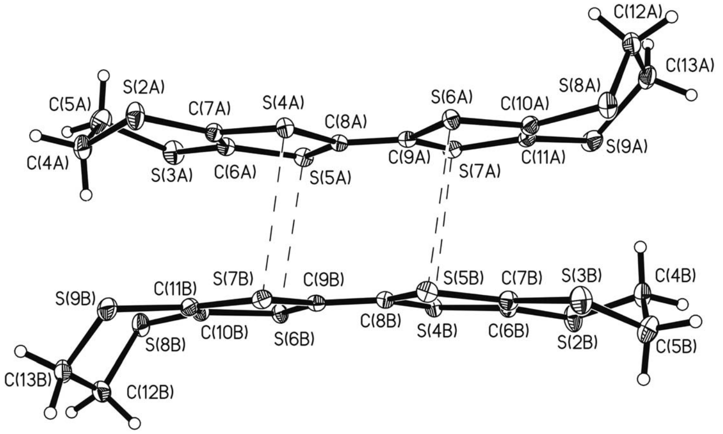

Fig. 6 Dimer formed by the BEDT-TTF radical-cations in the structure of (BEDT-TTF)[1,1′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$]. Dashed lines show intermolecular S⋯S contacts.

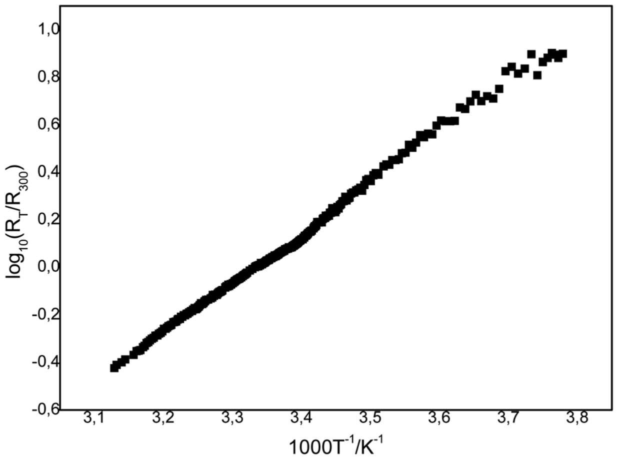

Fig. 7 Temperature dependence of resistivity in polycrystalline sample of (BEDT-TTF)[1,1′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$].

intermolecular contacts in the range 3.378–3.380 Å (the sum of the van der Waals radii S⋯S is 3.60 Å).[42] Slightly shortened S⋯S intermolecular contacts of the "side-by-side type" with a length of 3.628 Å were found between the dimers, thus forming a pseudo-layered architecture (Fig. 5). The intermolecular S(1)⋯S(5) contacts with a length of 3.633 (1) Å (which insignificantly exceed the sum of the van der Waals radii) were also found between the cationic and anionic layers. In the dimer (Fig. 6) formed by the BEDT-TTF donors, the distances between the averaged donor planes drawn through all sulfur atoms are 3.55 Å; the dihedral angle formed by the donor planes in the dimer is 0° by symmetry conditions. The donor molecules are non-planar and have a semi-chair conformation with the maximum deviation of sulfur atoms from the molecule plane of 0.14 Å (S(4) and S(5) atoms) and the maximum deviation of carbon atoms from this plane of 1.54 Å (C(12) atom).

The measurement of electric resistivity of polycrystalline sample of (BEDT-TTF)[1,1′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$] (Fig. 7) demonstrated that this salt is a semiconductor with the electrical conductivity at room temperature $\sigma_{293} \sim 6 \times 10^{-7}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$ and an activation energy of about 0.43 eV. The low electrical conductivity is due to both the stoichiometry of the simple salt and the irregularity of the BEDT-TTF layers and the strong dimerization of radical-cations in the stack.

Conclusions

The *C*-methylthio derivatives of cobalt bis(dicarbollide) as mixture of *rac*-[1,1′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ and *meso*-[1,2′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2]^-$ isomers were synthesized by reaction of anhydrous $CoCl_2$ with *nido*-carborane [7-MeS-7,8-$C_2B_9H_{11}]^-$ in the presence of potassium *tert*-butoxide. The structures of both isomers were studied using DFT quantum chemical calculations. For the *rac*-isomer, the optimized geometry corresponds to cisoid-rotamer stabilized by two intramolecular CH_{carb}⋯S(Me) hydrogen and two BH⋯S(Me) chalcogen bonds between the dicarbollide ligands, whereas for the *meso*-isomer the most preferable was found to be *gauche*-rotamer that is stabilized by stabilized by one CH_{carb}⋯S(Me) and three BH⋯S(Me) intramolecular bonds. It is noteworthy that the stabilization energy of in the *C*-methylthio derivatives of cobalt bis(dicarbolide) is significantly less than in the *B*-methylthio derivatives stabilized by exclusively CH_{carb}⋯S(Me) intramolecular bonds. Nevertheless, it was found that the geometry of the cisoid-rotamer is effectively realized in the X-ray structure of the (BEDT-TTF)[1,1′-$(MeS)_2$-3,3′-Co(1,2-$C_2B_9H_{10})_2$] salt which demonstrates semiconductor properties.

Experimental

Materials, instruments and general procedures

The cesium salt of 7-methylthio-*nido*-carborane was prepared according to the literature procedure.[26] Anhydrous $CoCl_2$ was prepared by dehydration of $CoCl_2\cdot 6H_2O$ using the standard procedure.[43] Tetrahydrofuran and 1,2-dimethoxyethane were dried by distillation over metallic sodium in the presence of benzophenone.[44] Other reagents were purchased from commercial suppliers and used without further purification.

Thin-layer chromatograms (DC Kieselgel F_{254} silicagel on aluminium plates, Merck) were visualized using 0.1% $PdCl_2$ in 3 M HCl(aq). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The ^1H, ^{11}B, and ^{13}C NMR spectra were collected using Bruker Avance-400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as the internal reference for ^1H NMR and ^{13}C NMR spectra. ^{11}B NMR spectrum was referenced using a $BF_3 \cdot Et_2O$ external standard. High-resolution mass spectrum was obtained on a Bruker Daltonics microOTOF II mass spectrometer.

Synthesis of $(Bu_4N)[1,1'(2')-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ and $(Me_4N)[1,1'(2')-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$

The reaction was carried out under argon atmosphere. To a solution of cesium salt of 7-methylthio-*nido*-carborane (0.60 g, 1.92 mmol) in dry 1,2-dimethoxyethane (50 ml), anhydrous $CoCl_2$ (2.49 g, 19.20 mmol) and potassium *tert*-butoxide (2.15 g, 19.20 mmol) were added. The mixture immediately warmed up and acquired dark green color. The reaction was stirred for 15 min at room temperature and heated under reflux for 30 h. The reaction mixture was allowed to cool to ambient temperature and filtered, the filtrate was evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 × 30 ml), dried over Na_2SO_4 and evaporated *in vacuo*. The desired product was obtained by the precipitation from water by water solution of tetramethyl- or tetrabutylammonium bromide as dark orange solid (65–80% yield). The spectral data for the tetrabutylammonium salt: ^1H NMR (acetone-d_6, ppm): 4.33 (1H, s, CH_{carb}), 4.29 (1H, s, CH_{carb}), 4.00 (2H, s, CH_{carb}), 3.45 (8H, Bu_4N^+), 2.40 (3H, s, SCH_3), 2.28 (3H, s, SCH_3), 1.84 (8H, Bu_4N^+), 1.45 (8H, Bu_4N^+), 1.00 (8H, Bu_4N^+), 2.7–0.8 (20H, m, B*H*). ^{13}C NMR (acetone-d_6, ppm): 67.4 (CH_{carb}), 63.6 ($CSCH_3$), 58.4 (Bu_4N^+), 23.4 (Bu_4N^+), 20.4 ($CSCH_3$), 19.4 (Bu_4N^+), 12.9 (Bu_4N^+). ESI HRMS for $[C_6H_{26}B_{18}CoS_2]^-$: calcd *m*/*z* 416.2613, obsd *m*/*z* 416.2603.

Synthesis of $K[1,1'-(2')-(MeS)_2-3,3'-Fe(1,2-C_2B_9H_{10})_2]$

To a solution of cesium salt of 7-methylthio-*nido*-carborane (0.45 g, 1.44 mmol) in dry THF (30 ml), anhydrous $FeCl_2$ (0.55 g, 4.30 mmol) and potassium *tert*-butoxide (0.81 g, 7.20 mmol) were added and heated under reflux for 2 days under argon atmosphere. The reaction mixture was allowed to cool to room temperature, evaporated to dryness *in vacuo* and treated with diethyl ether (50 ml) and water (50 ml). The organic layer was separated, evaporated to dryness *in vacuo* and treated with toluene (4 × 50 ml) and saturated aq. solution of K_2CO_3 (50 ml). The organic fraction was combined and evaporated *in vacuo* to obtain 0.15 g (47%) of red solid. ^{11}B NMR (acetone-d_6, ppm): 104.2, 29.4, 9.9, −4.2, −11.5, −31.8, −36.1, −384.2, −556.5.

Synthesis of $(BEDT\text{-}TTF)[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$

Crystals of the radical-cation salt $(BEDT\text{-}TTF)[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ were obtained by anodic oxidation of BEDT-TTF (2×10^{-3} M) in the presence of $(Me_4N)[1,1'(2')-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ (8×10^{-3} M) in 1,1,2-trilchloroethane–acetonitrile (12 : 1) mixture as a solvent under argon atmosphere in standard two-electrode H-cell with platinum electrodes separated by glass frit under galvanostatic conditions. The current applied was changed discretely on 0.05 μA per day from 0.20 to 1.50 μA.

Single crystal X-ray diffraction study

X-ray diffraction study of $(BEDT\text{-}TTF)[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ was carried out at 150 K with an Xcalibur, Eos diffractometer. The structure was solved by direct method followed by Fourier difference synthesis and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms using SHELXL software.[45,46] An empirical absorption correction of the experimental intensities was applied.[47] The hydrogen atoms were fixed in positions of ideal geometry.

Crystal and experimental data: $C_{16}H_{34}B_{18}CoS_{10}$, $M = 800.54$, monoclinic, $C2/c$, $a = 20.4048(6)$ Å, $b = 17.4839(6)$ Å, $c = 18.8696(6)$ Å, $\beta = 93.682(2)°$, $V = 830(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.58$ g cm^{-3}, $\mu = 1.150$ mm^{-1}, reflections observed/independent 20 623/9776, 409 parameters refined, $R = 0.037$ for 7827 reflections with $[F_0 > 4\sigma(F_0)]$.

Atomic coordinates, bond lengths, bond angles, and thermal parameters of the compound have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with a CCDC reference number 1967240. Bond lengths and selected angles are listed in Table S3.†

Electric resistivity measurements

The temperature dependence of electric resistivity of polycrystals of $(BEDT\text{-}TTF)[1,1'-(MeS)_2-3,3'-Co(1,2-C_2B_9H_{10})_2]$ was measured using two-contact-probe technique. The crystals were glued on the module with 2 platinum thin wire of diameter 15 μkm using conducting graphite paint. The module was mounted inside of stainless-steel thin-wall tube (diameter ∼11 mm), and the tube was slowly inserted to the transport helium jar with gradual cooling of the sample from 320 K to 265 K with cooling rate of 50–60 K h^{-1}.

Quantum-chemical calculations

The geometry optimizations were performed with the BP86 (ref. 48 and 49) functional with cc-pvdz basis set[50–53] without any symmetry restrictions using Gaussain09.[54] The tight SCF convergence criteria and ultrafine grid were applied. All minima on the PES were confirmed to have no negative values in their diagonalized force constants matrix. The transition state structures showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate. The QTAIM analysis was performed using the AIMALL program package[55] based on the wave function obtained by the BP86 calculations. The energies of non-covalent intramolecular interactions were calculated using the correlation between the binding energy (EBCP) and the value of the potential energy density function $V_C(r)$ in the corresponding critical point (3, −1): EBCP = $0.5V_C(r)$.[56,57] Such approach is widely used for energetic analysis of intermolecular interactions of different types.[24,40,41,58–60]

Conflicts of interest

There are no conflicts to declare.

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