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Tetrathiafulvalene-based radical cation salts with transition metal bis(dicarbollide) anions

Vladimir I. Bregadze[a], **Oleg A. Dyachenko**[b], **Olga N. Kazheva**[b],
Andrey V. Kravchenko[c], **Igor B. Sivaev**[a], **Vladimir A. Starodub**[d]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
Vavilov Str. 28, 119991 Moscow, Russia
[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
Semenov Av. 1, 142432, Chernogolovka, Moscow Region, Russia
[c] *V. N. Karazin Kharkiv National University, Department of Chemistry,*
Svoboda Sq. 4, 61077, Kharkiv, Ukraine
[d] *Institut Chemii Uniwersyteta Jana Kochanowskiego,*
ul. Świętokrzyska 15 G, 25-406 Kielce, Polska

Abstract. Radical cation salts based on derivatives of tetrathiafulvalene and sandwiched transition metal bis(dicarbollide) anions are of great interest for the development of new molecular conducting materials. The data on their synthesis, crystal structure, electrical and magnetic properties were reviewed. Effect of various substituents in the metallacarborane anion on the structure and physical properties of their tetratiafulvalene-based radical cation salts was analyzed. Relationships between the crystal structure and properties of the tetrathiafulvalene based radical cation salts containing sandwiched transition metal bis(1,2-dicarbollide) anions are discussed.

1. Introduction

Radical cation salts resulting from the oxidation of tetrathiafulvalene derivatives attract considerable interest in the preparation and study of molecular conducting and magnetic materials due to wide range of their electrical properties varying from dielectric to superconductors and ability to form magnetically ordered structures as well [1-5]. The standard approach to design of such materials is to make two-network solids formed by alternating layers of π-electron donors based on tetrathiafulvalene derivatives, which are responsible for electronic conduction, and layers of charge-compensating magnetic anions. The introduction of magnetic moments due to transition metals in these anions could result in indirect exchange interaction between the π-electrons of radical cations and the localized magnetic anions. In such a way conductive organic materials with magnetic ordering can be created [6,7].

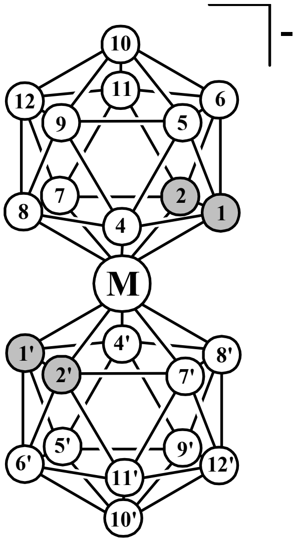
Conductivity in these materials occurs via the π-electron donor network made up of stacks or sheets of closely packed radical cations. The structure-directing role of counterions in formation of conductive properties of molecular conductors is of paramount importance because the crucial factor driving the multiplicity of conducting layer types is the docking of the donors onto the layer of anions, *i.e.*, some kind of complementarity of radical cation blocks and counterion units is needed. Single-crystal X-ray studies of tetrathiafulvalene based molecular conductors demonstrate a range of remarkable structural features such as conformational and charge ordering in the conducting radical cation layers as well as commensurate and incommensurate structural modulations mainly related to the positional ordering of the components of complex anion layers.

It suggests that subtle variations in the structure of the donor layers of these materials and consequently, change on their transport properties can be achieved by appropriately modifying the nature of their anionic layers. Organometallic chemistry provides a wide choice of metal complexes of various sizes and charges that can be used as charge-compensating counter-ions [8]. The bis(1,2-dicarbollide) complexes of transition metals $[3,3'\text{-M}(1,2\text{-C}_2B_9H_{10})_2]^-$ are known to demonstrate extraordinary stability due to the delocalized cluster bonding the transition metal with ligand orbitals and can be considered as charge-compensating counter-ions for synthesis of new radical cation-based molecular materials. These complexes could be easily modified by substitution of hydrogen atoms at carbon and boron atoms of the dicarbollide ligands for various non-hydrogen atoms and functional groups [9,10].

In this review structure and properties of the tetrathiafulvalene based radical cation salts containing sandwiched transition metal bis(1,2-dicarbollide) anions will be discussed. Pioneering researches in this field were carried out by Prof. Mingos in the mid-1990s [11], and the most recent results were obtained by the Russian-Ukraine collaborative team which is presented by the authors of this survey.

2. Transition metal bis(dicarbollide) complexes and their modification

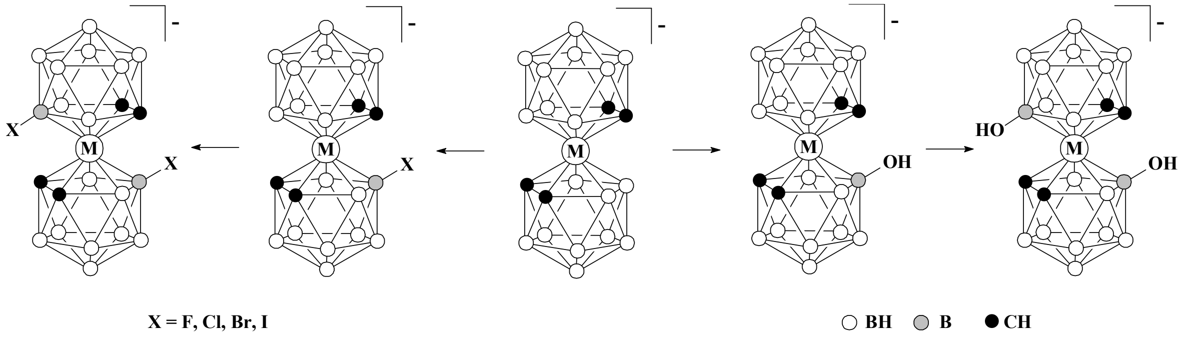
Radical cation salts containing sandwiched transition metal bis(1,2-dicarbollide) anions $[3,3'\text{-M}^{III}(1,2\text{-C}_2B_9H_{11})_2]^-$ (M = Cr, Fe, Co, Ni) (Scheme 1) as counter-ions are of great interest due to possibilities of variation of metal atoms and modification of the carborane ligands by an introduction of various substituents, as well as due to ability of these complexes to redox processes. The proper choice of the complex-forming metal allows one to vary magnetic properties of the complexes, whereas introduction of substituents which are capable to form intermolecular contacts with cation radicals gives possibility to create channels for exchange interactions between the magnetic subsystems. The last circumstance is important for preparation of magnetic structures with new properties.



Scheme 1. Atom numeration in the transition metal bis(1,2-dicarbollide) complexes $[3,3'\text{-M}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2]^-$ (M = Cr, Fe, Co, Ni).

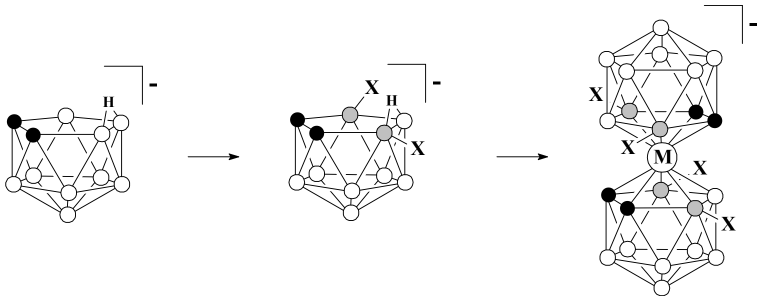
It should be noted that only four transition metals (chromium, iron, cobalt and nickel) are able to form stable bis(1,2-dicarbollide) complexes. Except nickel(III) bis(dicarbollide), which is easily oxidized to stable neutral nickel(IV) bis(dicarbollide) $[3,3'\text{-Ni}^{IV}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$, all other complexes have similar chemical properties [9,10,12]. At present, the chemistry of cobalt bis(1,2-dicarbollide) anion $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ is the most studied due to its diamagnetic character giving possibility to use NMR spectroscopy for characterization of its derivatives as well as for determination of their purity. Nevertheless, the development of modern NMR instruments allow to apply this technique for study of derivatives of paramagnetic iron bis(1,2-dicarbollide) [13].

Several strategies can be used for introduction of substituents in the metal bis(1,2-dicarbollide) complexes depending on the substitution position. The 8- and 8,8’-substituted derivatives can be prepared by electrophilic (halogens) or electrophile-induced nucleophilic (hydroxyl groups) substitution in the parent metal bis(dicarbollide) (Scheme 2) [14]. The same approach can be used for synthesis of the 8,8’,9,9’,12,12’-hexahalogen derivatives [14]. The iodine atoms can be readily replaced with alkyl or aryl groups by Pd-catalyzed cross-coupling reactions with the corresponding Grignard reagents [15,16].



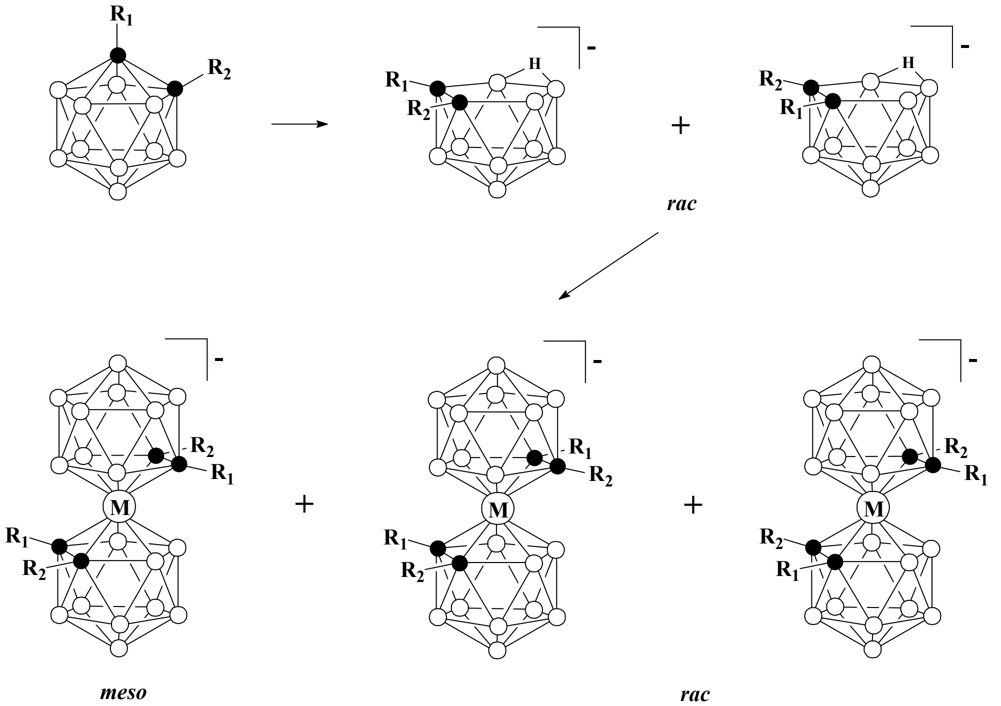
Scheme 2

Preparation of derivatives containing substituents at other positions of the bis(dicarbollide) system requires pre-synthesis of substituted carborane ligands followed by the metal complexation reaction. The 4,4’,7,7’-tetrahalogen derivatives can be obtained by halogenation of the parent *nido*-carborane followed by the metal complexation (Scheme 3) [17]. Since in this approach the metal atom is introduced in the last step, it can be used equally as for the synthesis of diamagnetic and paramagnetic complexes.



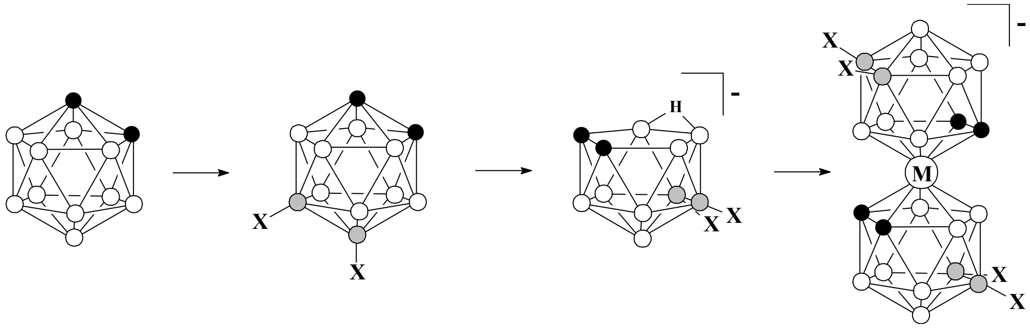
Scheme 3

C-substituted metal bis(dicarbollide) derivatives can be prepared by degradation of the corresponding C-substituted to the *nido*-form followed by metal complexation [9,10,18,19]. It should be noted that degradation of asymmetrically substituted carboranes produces a racemic mixture of the corresponding *nido*-carboranes, which in turn leads to a mixture of *rac*- and *meso*-complexes (Scheme 4).



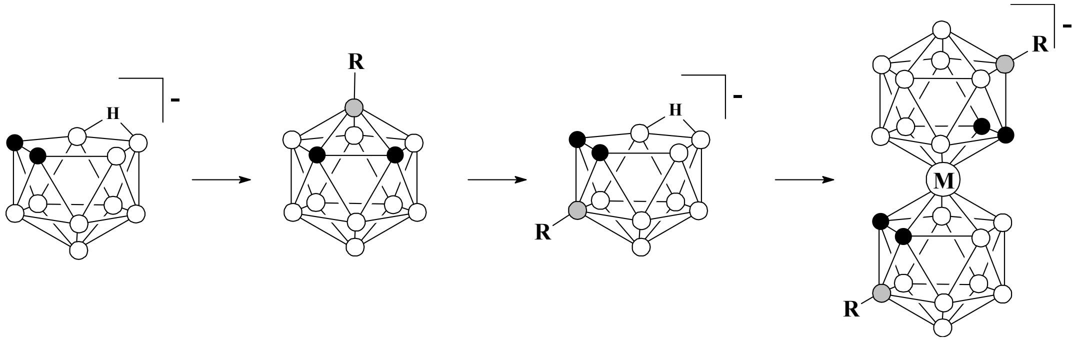
Scheme 4

The similar approach can be used for synthesis of the 9,9’(12’)-di- and 9,9’,12,12’-tetrahalogen derivatives starting from the corresponding 9-halogen and 9,12-dihalogen carboranes [14,20,21] (Scheme 5). And again, the degradation of 9-halogen-*ortho*-carboranes results in a racemic mixture of the corresponding *nido*-carboranes, which in turn leads to a mixture of *rac*- and *meso*- metal bis(dicarbollide) complexes. The related 9,9’(12’)-di- and 9,9’,12,12’-tetraaryl (alkyl) derivatives were prepared by Pd-catalyzed cross-coupling of 9-iodo and 9,12-diiodo carboranes with Grignard reagents followed by the cage decapitation and metal complexation [22,23].



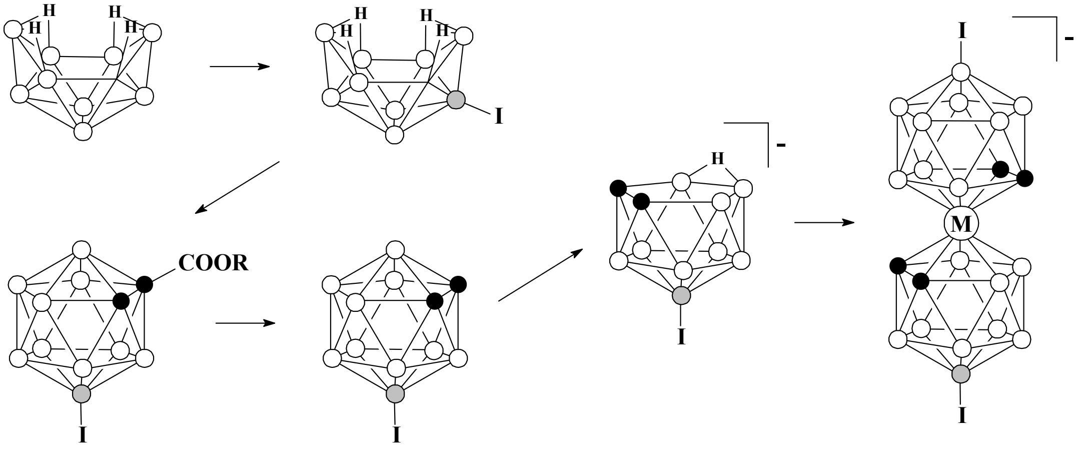
Scheme 5

The 6,6’-substituted metal bis(dicarbollide) complexes can be obtained from the corresponding 3-substituted *ortho*-carboranes using the cage decapitation - metal complexation strategy (Scheme 6) [24,25].



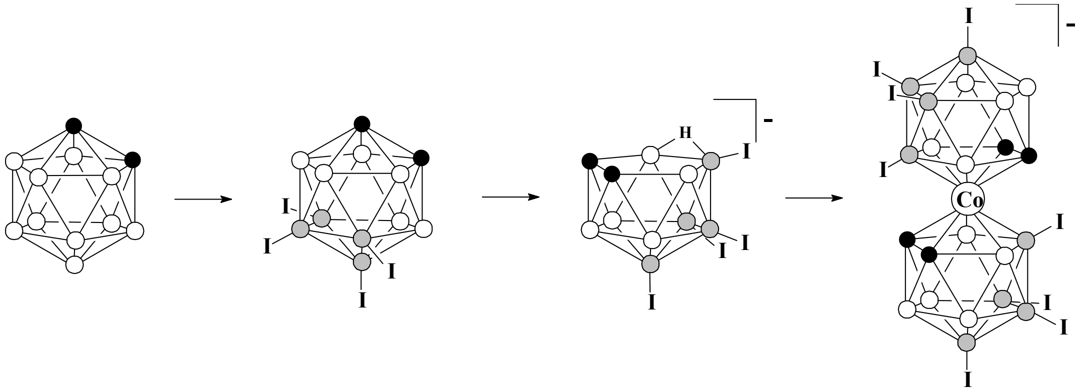
Scheme 6

Multistep synthesis of 10,10’-diiodo bis(dicarbollide) complexes of cobalt and nickel starting from decaborane was described recently [26] (Scheme 7).



Scheme 7

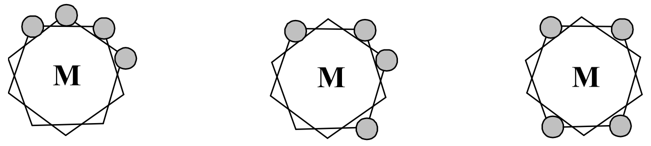
The maximum substitution degree is achieved by now in 8,8’,9,9’,10,10’,12,12’-octaiodo cobalt bis(dicarbollide), which was obtained from 8,9,10,12-tetraiodo-*ortho*-carborane using the decapitation - complexation strategy (Scheme 8) [27].



Scheme 8

The substituents in transition metal bis(dicarbollides) are not only capable to form intermolecular contacts in solids; their size and position also determine volume and shape of anion, that is important for formation of anionic sublattice. Thus, for example the maximum width and length of the 8,8’-diiodo cobalt bis(dicarbollide) anion [8,8’-I_2-3,3’-Co(1,2-$C_2B_9H_{10})_2]^-$ are approx. 7.5 and 10.2 Å [28], respectively, whereas the width and length of the of the 10,10’-diiodo cobalt bis(dicarbollide) anion [10,10’-I_2-3,3’-Co(1,2-$C_2B_9H_{10})_2]^-$ are 12.1 and 4.6 Å [26], respectively.

Mutual orientation of the dicarbollide ligands in the metallacarborane anions (Scheme 9) is another important factor determining crystal packing in molecular conductors. 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 the *cisoid* conformation (5.4 D for [3,3’-Co(1,2-$C_2B_9H_{11})_2]^-$ [29]) and an absence dipole moment in the *transoid* conformation. It is reasonably to suppose that crystals comprising bis(dicarbollide) anions in *transoid* and *cisoid* conformations having very different dipole moments should have different packing of these ions and different packing of counter ions as well.



cisoid ***gauche*** ***transoid***

Scheme 9. Mutual orientation of the dicarbollide ligands in the transition metal bis(1,2-dicarbollide) complexes.

Computational studies of relative energies of different rotamers of transition metal bis(dicarbollides) revealed that in the gas phase the *transoid* conformations of the cobalt(III) and iron(III) complexes are respectively by ~ 11 and 19 kJ/mol more stable than the *cisoid* ones [29,30], whereas for the nickel(III) complex the *cisoid* conformer is by ~ 8 kJ/mol more stable than the *transoid* one [30]. The *transoid* rotamer was found to be more stable for the chromium(III) complex as well [31]. However, the difference in energy of conformers is rather low that often results in stabilization of less preferable conformations in the solid state. Thus, for example only 10 % of cobalt(III) bis(dicarbollide) complexes in the solid state present *transoid* conformation [29]. The substitution can increase stability of an initial rotamer or, on the contrary, stabilize other one. For example, for 6,6’-dialkyl nickel(III) bis(dicarbollide) the *transoid* conformation is by ~ 11 kJ/mol more stable than *cisoid* one [25].

Synthesis, crystal structure and physical properties of the tetrathiafulvalene based radical cation salts with transition metal bis(dicarbollide) anions will be discussed below.

3. Radical cation salts of transition metal bis(dicarbollide) anions

a.) Transition metal bis(dicarbollide) salts with TTF radical cations

The first cation radical salts $(TTF)[3,3'\text{-}M^{III}(1,2\text{-}C_2B_9H_{11})_2]^-$ (M = Cr (**1**), Fe (**2**), Ni (**3**)) were reported by Mingos et al. in 1994 [32]. Compounds **1** and **2** were prepared by precipitation of the corresponding bis(dicarbollide) complexes with $(TTF)^{\cdot+}Cl^{-}$, followed by crystallization from acetone-ethanol mixture, whereas compound **3** was obtained by direct oxidation TTF with $[3,3'\text{-}Ni^{IV}(1,2\text{-}C_2B_9H_{11})_2]$ in dichloromethane. Later we synthesized the cobalt analogue $(TTF)^{\cdot+}[3,3'\text{-}Co^{III}(1,2\text{-}C_2B_9H_{11})_2]^-$ (**4**) by anodic oxidation of TTF in the presence of $Na[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ under galvanostatic conditions [33]. Despite similar composition of these cation radical salts and close size of the bis(dicarbollide) anions in **1**-**4**, their structures are different. The structure of **1** are formed by alternating chains of $(TTF)^{\cdot+}$ cations and $[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{11})_2]^-$ anions, whereas complexes **2-4** are isostructural and contain discrete stacked dimers of $(TTF)^{\cdot+}$ cations (Figure 1).

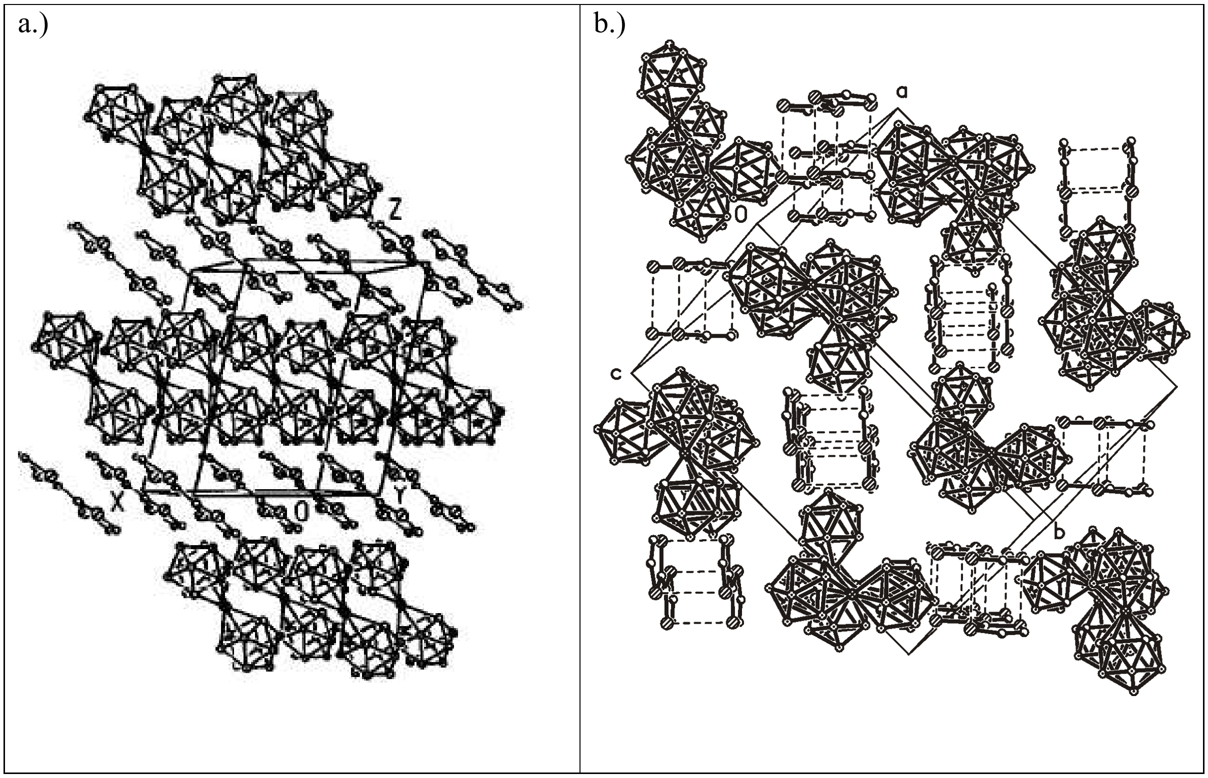


Figure 1. The crystal packing of (a) (TTF)[3,3'-Cr(1,2-$C_2B_9H_{11})_2$] (**1**) (reproduced with permission from Ref. [32]. Copyright © (1994) Elsevier Masson SAS) and (b) (TTF)[3,3'-M(1,2-$C_2B_9H_{11})_2$] (M = Fe, Ni, Co) (**2-4**) (reproduced with permission from Ref. [33]. Copyright © (2006) Elsevier Masson SAS).

The difference in the structures of these compounds can be explained by different orientation of the dicarbollide ligands in the metallacarborane anions: in **1** the dicarbollide ligands adopt *transoid* conformation, whereas in **2-4** they are in *cisoid* arrangement. As expected, the conductivity of the obtained materials is determined by their crystalline structure. Complex **1** is a narrow-gap semiconductor ($\sigma_{RT} = 3\cdot10^{-4}$ S cm^{-1}, activation energy 0.16 eV), whereas complexes **2** and **3** are insulators ($\sigma_{RT} < 10^{-7}$ S cm^{-1}), that is consistent with the presence of the isolated (TTF$^{\cdot+}$)$_2$ dimers in the crystal structure. No cooperative magnetic behaviour was observed in complexes **1-3**. The magnetic susceptibilities of these complexes follow the Curie-Weiss Law $\chi = C/(T\text{-}\theta)$, with θ values of -2.5, -2.0 and 1.5 K, respectively, indicating negligible interaction between the unpaired spins in the solids.

The related complex containing iodine atoms at positions 8 and 8' of the cobalt bis(dicarbollide) anion, (TTF)[8,8'-I_2-3,3'-Co(1,2-$C_2B_9H_{10})_2]^-$ (**5**), was prepared by anodic oxidation of TTF in the presence of K[8,8'-I_2-3,3'-Co(1,2-$C_2B_9H_{10})_2$] and 18-crown-6 [34]. The anions adopt usual for the 8,8'-dihalogen derivatives *transoid* conformation additionally stabilized by intramolecular B-I···H-C_{carb} hydrogen bonding and form chains along the *a* and *c*-axes, whereas single TTF radical cations are located in the between of the anion chains (Figure 2).

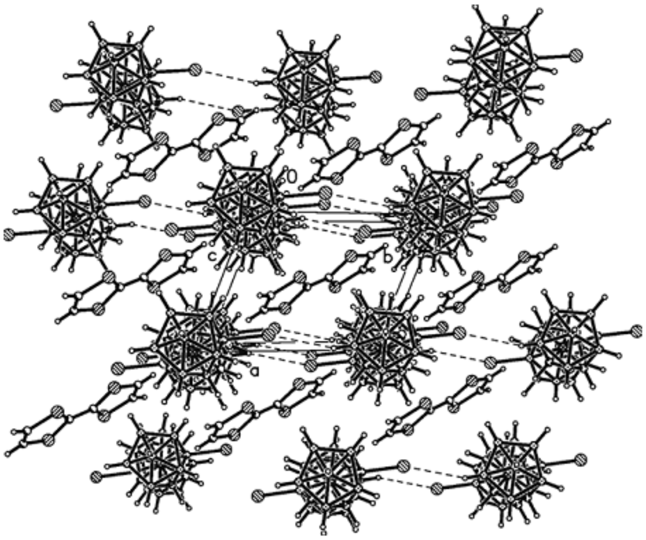


Figure 2. The crystal packing of (TTF)[8,8'-I_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**5**). Reproduced with permission from Ref. [34]. Copyright © (2009) Elsevier Masson SAS.

Despite the structure excluding the direct interaction of the radical cations, complex **5** has rather high electric conductivity (σ_{RT} = 0.05 S cm^{-1}, activation energy 0.4 eV), that can be explained by high carrier mobility.

The complex containing iodine atoms at positions 9,9',12 and 12' of the cobalt bis(dicarbollide) anion, (TTF)[9,9',12,12'-I_4-3,3'-Co(1,2-$C_2B_9H_9$)$_2$] (**6**), was prepared by anodic oxidation of TTF in the presence of K[9,9',12,12'-I_4-3,3'-Co(1,2-$C_2B_9H_9$)$_2$] and 18-crown-6 [21]. The anions adopt *cisoid* conformation and are linked to each other by the short intermolecular I···I bonds. The radical cation and anion layers are alternating along the *b* axis, the radical cation layer is formed by stacked ($TTF^{\cdot+}$)$_2$ dimers with the TTF units in each dimer being virtually eclipsed at interplanar separation of 3.48 Å without short contacts between the dimers. The anion and cation layers are connected by short intermolecular I···S bonds (Figure 3). Complex **6** is semiconductor with σ_{RT} = 6•10^{-7} S cm^{-1} (activation energy of 0.24 eV) that is somewhat larger than in the related salt with the parent cobalt bis(dicarbollide) **4**, but is five orders of magnitude smaller than the conductivity of the 8,8'-diiodo derivative **5**.

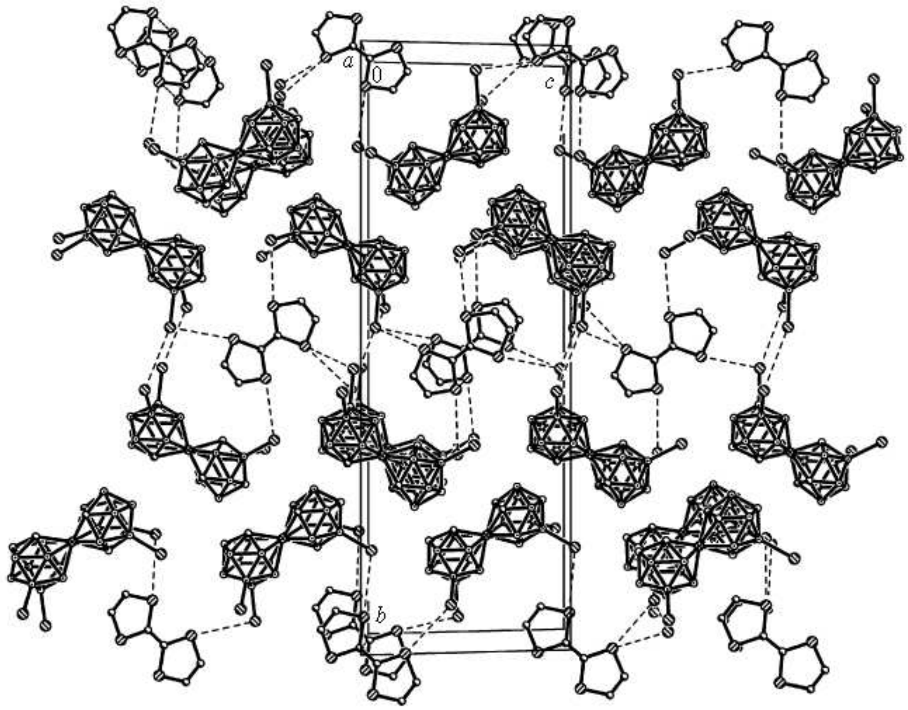


Figure 3. The crystal packing of (TTF)[9,9’,12,12’-I_4-3,3’-Co(1,2-$C_2B_9H_9$)$_2$] (**6**). Reproduced with permission from Ref. [21]. Copyright © (2010) Springer Science and Business Media.

The interesting results were obtained with C,C’-disubstituted iron bis(dicarbollide). Reaction of Na[1,1’-(thiophene-2-yl)-3,3’-Fe(1,2-$C_2B_9H_{10}$)$_2$] with (TTF)$^{\cdot+}$Cl$^-$ in aqueous solution followed by crystallization from acetone-dichloromethane/toluene at -20 ºC gave (TTF)[1,1’-(thiophene-2-yl)-3,3’-Fe(1,2-$C_2B_9H_{10}$)$_2$]*toluene (**7**) [35]. Complex **7** is an insulator ($\sigma_{RT} < 10^{-7}$ S cm^{-1}). The TTF$^{\cdot+}$ cations in **7** form staked dimers; the each (TTF$^{\cdot+}$)$_2$ dimer is effectively isolated from other dimers by anions and toluene solvate molecules which thus disrupt the formation of extended TTF stacks suitable for electrical conduction.

Slow crystallization of **7** from acetone-ethanol resulted in formation of the mixed valence complex (TTF)$_5$[1,1’-(thiophene-2-yl)-3,3’-Fe(1,2-$C_2B_9H_{10}$)$_2$] (**8**) [35]. The crystal structure of **8** contains extended columns of stacked (TTF$^{\cdot+}$)$_3$ trimers propagating along the *a* axis with interplanar separation between the TTF units in trimers of 3.47 Å and the distances between adjacent trimers of 3.54 Å. Along the *c* axis the trimers linked by short S···S contacts (3.56 Å) with other TTF unit which is practically perpendicular to the TTF units in the trimers, forming continuous two-dimensional layer of linked TTF trimers. The remaining TTF unit is involved in S···S bonding with the thiophene-2-yl substituents of the iron bis(dicarbollide) anion (Figure 4).

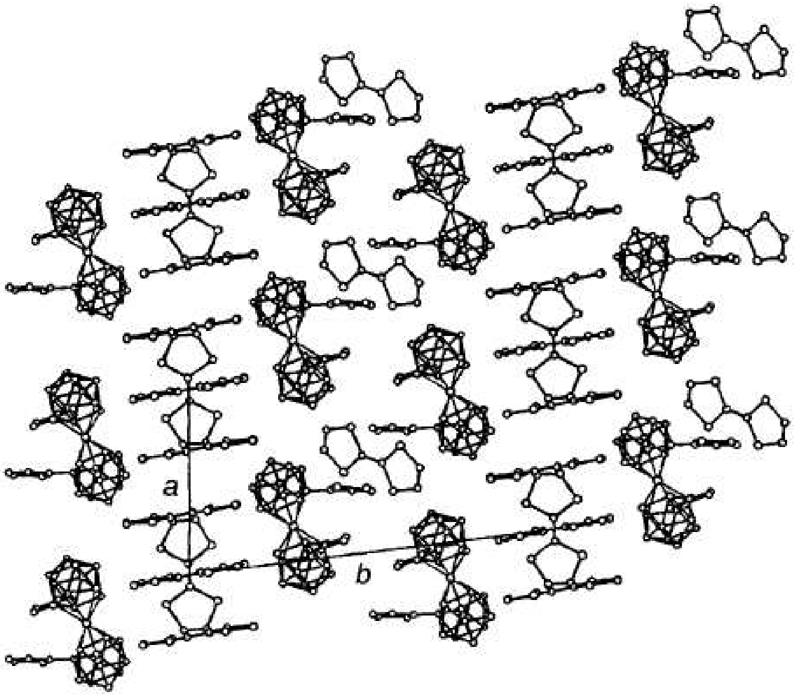


Figure 4. The crystal packing of $(TTF)_5[1,1'\text{-(thiophene-2-yl)-3,3'-Fe}(1,2\text{-}C_2B_9H_{10})_2]$ (**8**).

The complex **8** is semiconductor with $\sigma_{RT} = 2{\bullet}10^{-3}$ S cm^{-1} (activation energy of 0.22 eV). The corrected magnetic susceptibilities of complexes **7** and **8** follow the Curie-Weiss Law $\chi = C/(T\text{-}\theta)$, with θ values of 0.5 and 1.9 K, respectively. The magnetic contributions of the radical cations in both complexes equal zero that is well consistent with their structure data.

b.) Transition metal bis(dicarbollide) salts with BEDT-TTF radical cations

The transition metal bis(dicarbollide) salts with BEDT-TTF radical cations are the most studied. The 1:1 complex $(BEDT\text{-}TTF)^{\cdot+}[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ (**9**) was obtained by electrochemical oxidation of BEDT-TTF in the presence of $Na[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ [33]. In the structure of **9** the cationic and anionic layers alternate along the *b* axis (Figure 5). The dicarbollide ligands in the cobalt bis(dicarbollide) anion adopt *cisoid* conformation similar to found in the structure of complex **4**. The radical cations form stacked $(BEDT\text{-}TTF^{\cdot+})_2$ dimers with the BEDT-TTF units in each dimer being virtually eclipsed with short interplanar S···S contacts of 3.40-3.45 Å. Complex **9** is semiconductor with $\sigma_{RT} = 5{\cdot}10^{-4}$ S cm^{-1} and activation energy 0.18 eV.

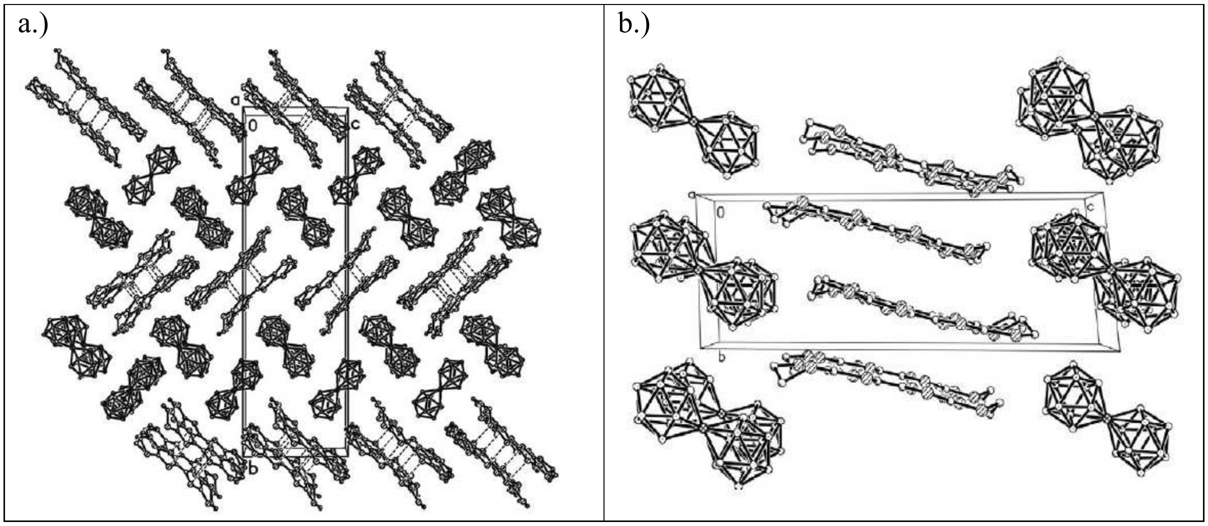


Figure 5. The crystal packing of (a) (BEDT-TTF)[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] (**9**) (reproduced with permission from Ref. [33]. Copyright © (2006) Elsevier Masson SAS) and (b) (BEDT-TTF)$_2$[3,3'-M(1,2-$C_2B_9H_{11}$)$_2$] (M = Cr, Fe, Co) (**10-12**) (reproduced with permission from Ref. [37]. Copyright © (2012) Elsevier Masson SAS).

The 2:1 complexes (BEDT-TTF)$_2$[3,3'-M(1,2-$C_2B_9H_{11}$)$_2$]$^-$ (M = Cr (**10**), Fe (**11**), Co (**12**)) were prepared by the oxidation o BEDT-TTF with hydrogen peroxide in the presence of acidic form of chromium bis(dicarbollide) H[3,3'-Cr(1,2-$C_2B_9H_{11}$)$_2$] [36] or anodic oxidation of BEDT-TTF in the presence of (Me_4N)[3,3'-Fe(1,2-$C_2B_9H_{11}$)$_2$] [37] and Na[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] [38], respectively. The complexes **10**-**12** are isostructural and contain layers of the BEDT-TTF radical cations and metallacarborane anions alternating along the c axis. In the conducting layer the radical cations are packed like β'-type [39] forming nearly regular stacks (Figure 5). All these complexes are semiconductors with $\sigma_{RT} = 2\cdot10^{-3}$, $1.5\cdot10^{-2}$ and $1\cdot10^{-1}$ S cm^{-1}, respectively. The increase of electric conductivity in the Cr-Fe-Co bis(dicarbollide) series correlates well with the reduction of the unit cell volume and can be explained by the difference in size of the transition metal cations.

The temperature dependence of magnetic susceptibility of complex **10** follows the Curie-Weiss law $\chi = C/(T-\theta)$, with θ value of -1.1 K indicating the presence of weak antiferromagnetic interactions. The effective magnetic moment value of 3.6 μ_B is close to that in Cs[3,3'-Cr(1,2-$C_2B_9H_{11}$)$_2$] (3.8 μ_B) demonstrating apparent absence of magnetic contribution from the BEDT-TTF radical cations. The temperature dependence of magnetic susceptibility of complex **11** is described the best by a model of two non-interacting paramagnetic centers $\chi = C_1/(T_1-\theta_1) + C_2/(T_2-\theta_2)$ (C_1 = 0.3361 emu K/mol, C_2 = 0.3442 emu K/mol, θ_1 = 0.49 K, θ_2 = 0 K), where the first term describes weak ferromagnetic interactions of the (BEDT-TTF$^{\cdot+}$)$_2$ dimers in the radical cation stacks and the second term is related to the anion susceptibility.

As in the case of the TTF radical cation salts, the introduction of halogen substituents in the bis(dicarbollide) anions can results in weak interactions between the cationic and anionic sublattices of the BEDT-TTF radical cation salts. In the structure of (BEDT-TTF)[8,8'-Br_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**13**) the BEDT-TTF cations and the cobaltacarborane anions alternate forming mixed stacks connected by short intermolecular S···Br contacts of 3.77 Å (Figure 6) [40]. These short contacts could act as channels of exchange interactions or electron transfer. The room-temperature electrical conductivity of complex **13** ($\sigma_{RT} = 1.5\cdot10^{-3}$ S cm^{-1}) is somewhat higher than in the parent complex **9**; the activation energy in the range of 130-300 K is 0.08 eV and decreases to 0.01 eV on cooling to 30-70 K, that can be explained by low-temperature lattice contraction and further shortening of S···Br contacts.

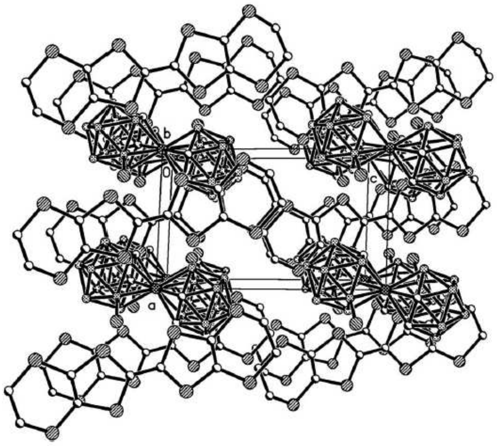


Figure 6. The crystal packing of (BEDT-TTF)[8,8'-Br_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**13**). Reproduced with permission from Ref. [40]. Copyright © (2008) Elsevier Masson SAS.

The similar effect was found the related complex (BEDT-TTF)[8,8'(7)-Cl_2($Cl_{0.09}$)-3,3'-Co(1,2-$C_2B_9H_{9.91}$)(1',2'-$C_2B_9H_{10}$)] (**14**) where the BEDT-TTF cations and the cobaltacarborane anions alternate along the a axis forming mixed stacks connected by short intermolecular S···Cl contacts of 3.33-3.55 Å [41]. The room-temperature electrical conductivity of complex **14** equals 2 S cm^{-1}, with activation energy of 0.09 eV in the range of 125-140 K, that decreases to 0.01 eV on cooling to 12-40 K. It should be noted that in the both structures the 8,8'-dihalogen cobalt bis(dicarbollide) ligands adopt *transoid* conformation. The situation is changed dramatically in the case of the mixed salt (BEDT-TTF)[8,8'-$Br_{0.75}Cl_{1.25}$-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**15**), which is isostructural with complex **14** [41]. However, in this case only the [8-Br-8'-Cl-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$ anion adopts *transoid* conformation, whereas the [8,8'-Cl_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$]$^-$

anion has *gauche* conformation. As the result, the room-temperature electrical conductivity for **15** is reduced to $1{\cdot}10^{-5}$ S cm^{-1} and the activation energy increases to 0.26 eV.

It should be mentioned that the introduction in metallacarborane anion of small substituent, such as hydroxy group, does not produce significant effect on structure and electrical conductivity of the radical cation salts. For example, the complex (BEDT-TTF)[8-OH-3,3'-Co(1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)] (**16**) is isostructural to the parent complex **9** [42]. Similarly to **9** the complex **16** is semiconductor with $\sigma_{RT} = 7{\cdot}10^{-4}$ S cm^{-1} and the activation energy of 0.25 eV.

Non-layered structure with alternation of metallacarborane anions and the BEDT-TTF radical cation pairs was found also in radical cation salt with different substituents in the cobalt bis(dicarbollide) anion (BEDT-TTF)[8-I-8-Ph-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**17**). The complex **17** is semiconductor with the room-temperature electric conductivity of $3{\cdot}10^{-7}$ S cm^{-1} [43].

The introduction of halogens at positions 9 and 12 of the cobalt bis(dicarbollide) anion in complex (BEDT-TTF)[9,9'(12')-I_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**18**) results in formation of short intermolecular S···I contacts of 3.67 Å between the cationic and anionic sublattices, however in spite of the alternation of the radical cation and anion layers along the *b* axis the radical cation layer is formed by the BEDT-TTF dimers, which are not linked together and do not form a conducting layer (Figure 7) [21]. The complex **18** is semiconductor with room-temperature conductivity $\sigma_{RT} = 3{\bullet}10^{-5}$ S cm^{-1} and activation energy of 0.29 eV.

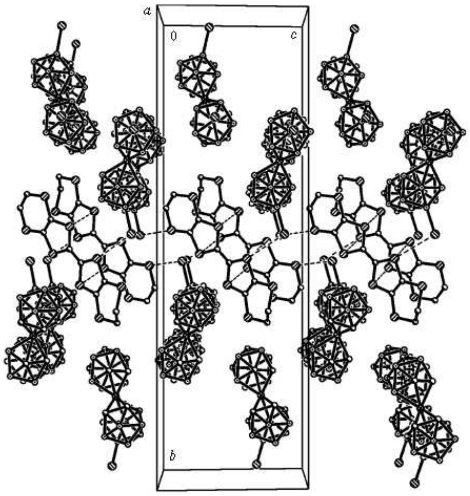


Figure 7. The crystal packing of (BEDT-TTF)[9,9'(12')-I_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (**18**). Reproduced with permission from Ref. [21]. Copyright © (2010) Springer Science and Business Media.

The interesting features were found in the series of 2:1 complexes of 8,8'-dihalogen cobalt bis(dicarbollides) (BEDT-TTF)$_2$[8,8'-X$_2$-3,3'-Co(1,2-C$_2$B$_9$H$_{10}$)$_2$] (X = Cl (**19**) [44], Br (**20**) [40], I (**21**) [34]). All these compounds are isostructural with cationic and anionic layers alternating along the *c* axis. The anions in all complexes adopt *transoid* conformation stabilized by formation of the B-X···H-C intramolecular bonds between the dicarbollide ligands. The BEDT-TTF cations in the conducting layer are packed like β-type [39] (Figure 8).

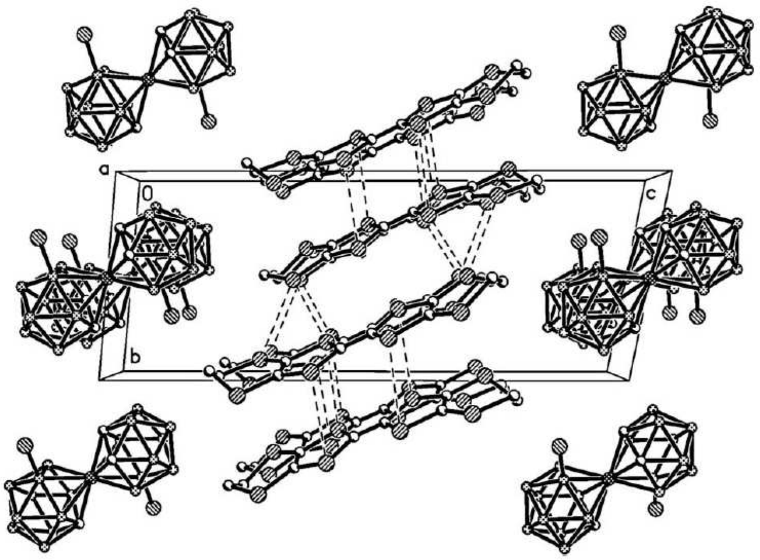


Figure 8. The crystal packing of (BEDT-TTF)$_2$[8,8'-X$_2$-3,3'-Co(1,2-C$_2$B$_9$H$_{10}$)$_2$] (X = Cl, Br, I) (**19-21**). Reproduced with permission from Ref. [40]. Copyright © (2008) Elsevier Masson SAS.

The decrease in the substituent size in this series results in more dense crystal packing with systematic shortening of distances between the BEDT-TTF units in dimers as well as between the dimers themselves (Table 1). The electric conductivity σ_{RT} of the most densely packed complex **19** is 1.5 S cm^{-1} with activation energy E$_a$ =0.12 eV.

Table 1. Some structural characteristics and electric conductivities of complexes **19-21**.

Complex	Unit cell volume, V/Å^3	BEDT-TTF intra-dimer distance, Å	BEDT-TTF inter-dimer distance, Å	Electric conductivity, σ_{293}/S•cm^{-1}
19	1128.9(3)	3.54	3.63	1.5
20	1155.8(4)	3.59	3.75	5•10^{-4}
21	1222.3(2)	3.64	3.84	6•10^{-3*}

*polycrystalline sample

The similar crystal packing of β-type was found also in the isostructural the 8-iodo complex $(BEDT-TTF)_2[8-I-3,3'-Co(1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$ (**22**). The room-temperature conductivity and activation energy for complex **22** are 0.1 S cm^{-1} and 0.05 eV, respectively [38].

The interesting structure was found in the 2:1 complex with C,C'-disubstituted iron bis(dicarbollide) $(BEDT-TTF)_2[1,1'-(thiophene-2-yl)-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ (**23**) [36]. In common with most BEDT-TTF salts, complex **23** has a layered structure. However, in this structure the metallacarborane anions form double layers with all the thiophene substituents essentially directed towards each other and away from the BEDT-TTF layers precluding formation of S···S interactions between the anionic and cationic layers (Figure 9). Complex **23** is narrow gap semiconductor with σ_{RT} = 0.5 S cm^{-1} and E_a = 0.046 eV. The temperature dependence of magnetic susceptibility follows the Curie-Weiss law $\chi = C/(T-\theta)$, with θ value of 1.6 K indicating the presence of weak ferromagnetic interactions [36].

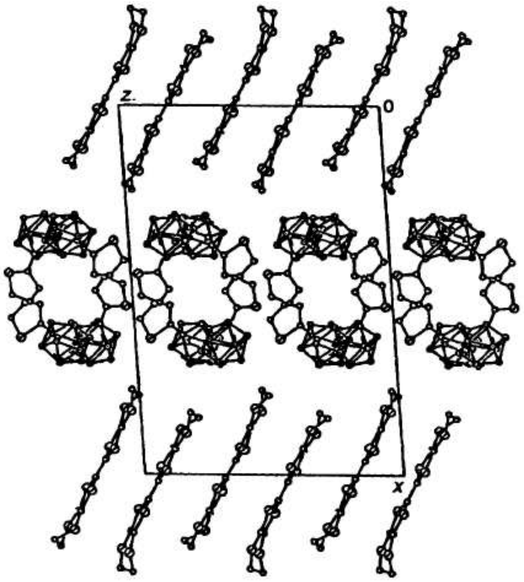


Figure 9. The crystal packing of $(BEDT-TTF)_2[1,1'-(thiophene-2-yl)-3,3'-Fe(1,2-C_2B_9H_{10})_2]$ (**23**).

c.) Cobalt bis(dicarbollide) salts with BMDT-TTF radical cations

Two different structural types were obtained for the BMDT-TTF radical cation salts with transition metal bis(dicarbollides). The 1:1 complex $(BMDT-TTF)[3,3'-Co(1,2-C_2B_9H_{11})_2]$ (**24**) was obtained by electrochemical oxidation of BMDT-TTF in the presence of $Na[3,3'-Co(1,2-C_2B_9H_{11})_2]$ and 15-crown-5 [38]. In the structure of **24** the BMDT-TTF cations and the cobaltacarborane anions alternate along the *ab* diagonal forming mixed stacks (Figure 10). The cobalt bis(dicarbollide) anions adopt *transoid* conformation. Complex **24** is narrow gap semiconductor with σ_{RT} = 0.01 S cm^{-1} and E_a = 0.04 eV.

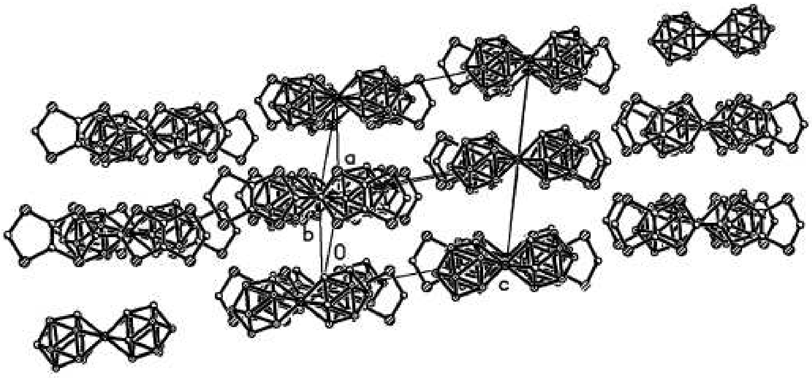


Figure 10. The crystal packing of (BMDT-TTF)[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] (**24**). Reproduced with permission from Ref. [38]. Copyright © (2007) Elsevier Masson SAS.

As was mentioned above, the introduction of hydroxy group in the cobalt bis(dicarbollide) anion does not produce significant effect on structure and electrical conductivity of the radical cation salts; complex (BMDT-TTF)[8-OH-3,3'-Co(1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)] (**25**) was found to be isostructural with the related complex **24** with the parent cobalt bis(dicarbollide). The room temperature conductivity of the complex **25** is $1.5 \cdot 10^{-7}$ S cm^{-1} [42].

Other structural type was found in the series of 8,8'-dihalogen cobalt bis(dicarbollides) (BMDT-TTF)$_4$[8,8'-X_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$] (X = Cl (**26**) [44], Br (**27**) [40], I (**28**) [34]). All these compounds are isostructural with cationic and anionic layers alternating along the *c* axis. The anions in all complexes adopt *transoid* conformation stabilized by formation of the B-X···H-C intramolecular bonds between the dicarbollide ligands. The BMDT-TTF cations in the conducting layer are packed like α-type [45]. The BMDT-TTF stacks in the conducting layer are not uniform. One type of stacks is formed by the A and B donor molecules alternating in the -A-A-B-B- order and the other one is formed by the C and D donor molecules in the -C-C-D-D- order (Figure 11).

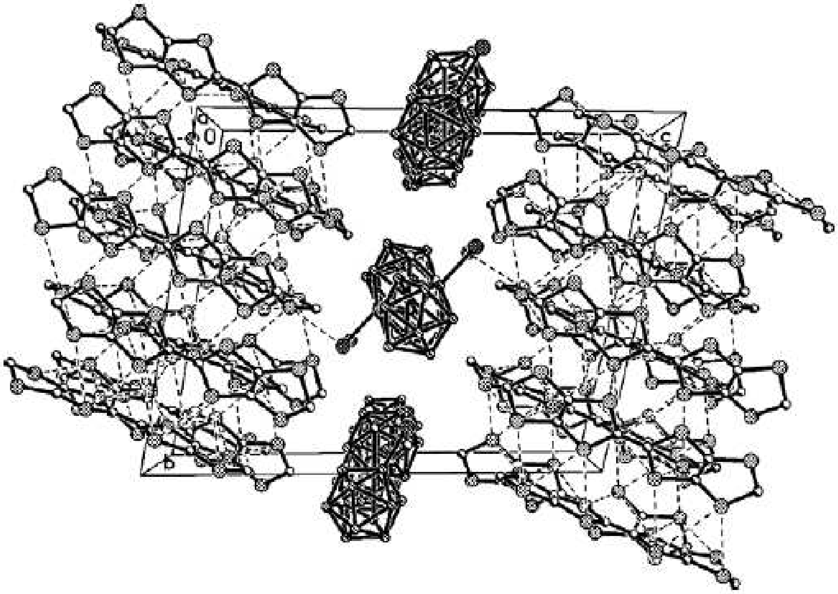


Figure 11. The crystal packing of (BMDT-TTF)$_4$[8,8'-X$_2$-3,3'-Co(1,2-C$_2$B$_9$H$_{10}$)$_2$] (X = Cl, Br, I) (**26-28**). Reproduced with permission from Ref. [34]. Copyright © (2009) Elsevier Masson SAS.

As in the case of the BEDT-TTF 2:1 complexes, the decrease in the substituent size in this series results in more dense crystal packing with systematic shortening of distances between the BMDT-TTF units in dimers as well as between the dimers themselves (Table 2). All these complexes are narrow-gap semiconductors with σ_{RT} = 2.0, 1.0 and 0.25 S cm^{-1} and E$_a$ = 0.025, 0.05 and 0.044 eV, respectively.

Table 2. Some structural characteristics and electric conductivities of complexes **26-28**.

Complex	Unit cell volume, V/Å^3	BMDT-TTF distance, Å						Electric conductivity, σ_{293}/S•cm^{-1}
		A-A	B-B	A-B	C-C	D-D	C-D	
26	3285.5(5)	3.51	3.44	3.62	3.50	3.44	3.61	2.0
27	3346.8(4)	3.57	3.49	3.59	3.55	3.51	3.67	1.0
28	3372.1(4)	3.58	3.50	3.68	3.56	3.52	3.69	0.25

The similar crystal packing of α-type was found in the isostructural the 8,8'-bromo/hydroxy complex (BEDT-TTF)$_2$[8,8'-Br$_{1.16}$(OH)$_{0.72}$-3,3'-Co(1,2-C$_2$B$_9$H$_{10.06}$)$_2$] (**29**). The room-temperature conductivity for complex **29** are 0.5 S cm^{-1} with activation energy E_a = 0.02 eV at 140-293 K and 0.004 eV at 16-35 K [41].

d.) Cobalt bis(dicarbollide) salts with TMTTF radical cations

Two TMTTF radical cation salts with substituted cobalt bis(dicarbollides) (TMTTF)[8-HO-3,3'-Co(1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)] (**30**) [42] and (TMTTF)[8,8'-Cl_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$]$_2$ (**31**) [43] were described. In the 1:1 complex **30** the TMTTF radical cations are isolated from each other by the cobaltacarborane anions disrupting the formation of the donor stacks suitable for electrical conduction (Figure 12). In the 1:2 complex **31** the TMTTF radical cations are isolated each from other even more effectively. The 8,8'-dichloro cobalt bis(dicarbollide) anions adopt gauche conformation and are turned to the TMTTF radical cations by chlorine atoms (Figure 12). The both salts are insulators.

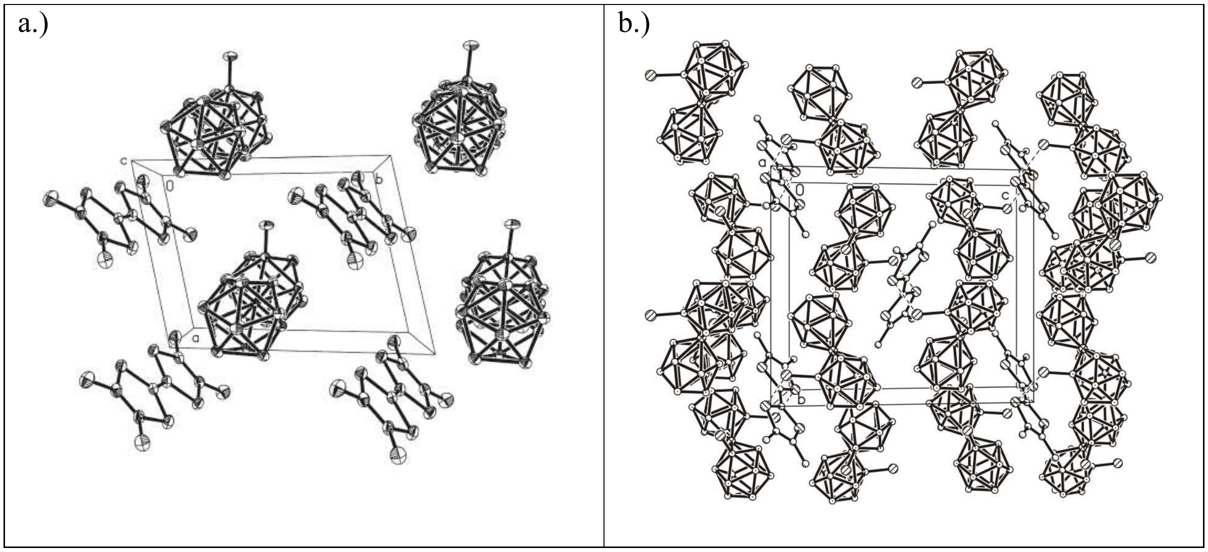


Figure 12. The crystal packing of (a) (TMTTF)[8-HO-3,3'-Co(1,2-$C_2B_9H_{10}$)(1',2'-$C_2B_9H_{11}$)] (**30**) and (b) (TMTTF)[8,8'-Cl_2-3,3'-Co(1,2-$C_2B_9H_{10}$)$_2$]$_2$ (**31**). Reprinted with permission from Ref. [42]. Copyright (2011) American Chemical Society.

e.) Transition metal bis(dicarbollide) salts with TMTSF radical cations

Two TMTSF radical cation salts with transition metal bis(dicarbollide) anions (TMTSF)$_2$[3,3'-M(1,2-$C_2B_9H_{11}$)$_2$] (M = Fe (**32**) [38] and Co(**33**) [33]) were prepared by electrochemical oxidation of TMTSF in the presence of iron and cobalt bis(dicarbollide), respectively. The complexes are isostructural. The bis(dicarbollide) anions adopt *transoid* conformations. The TMTSF radical cations and the metallacarborane anions are packed in stacks along the *a*-axis forming layers that are parallel to the *ab*- and *ac*-planes and alternate along the *b* and *c*-axes (Figure 13).

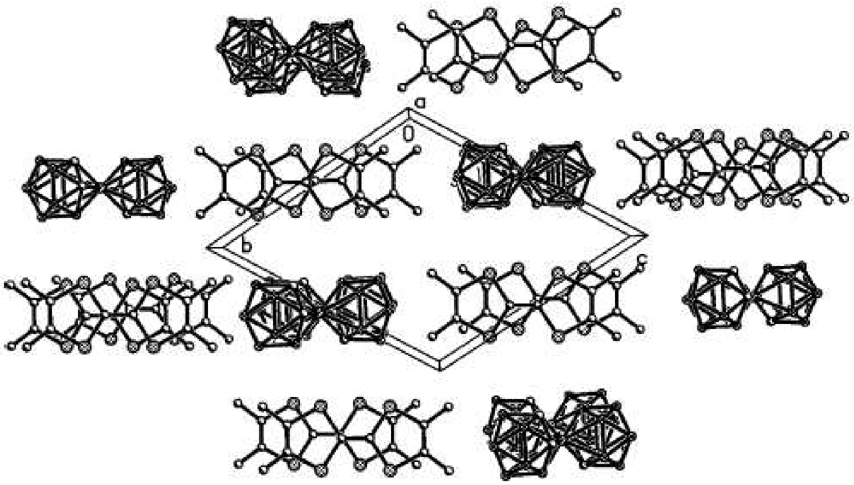
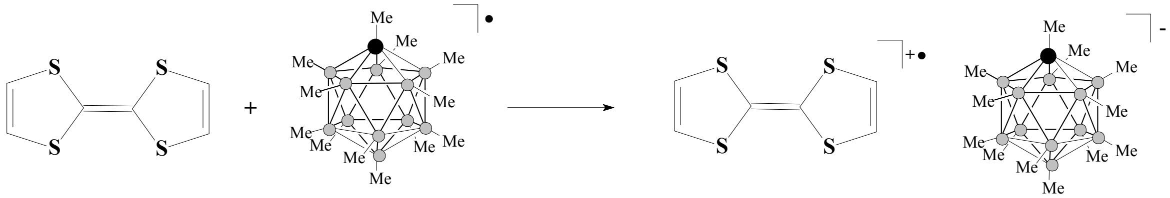


Figure 13. The crystal packing of $(TMTSF)_2[3,3'\text{-}M(1,2\text{-}C_2B_9H_{11})_2]$ (M = Fe, Co) (**32, 33**). Reproduced with permission from Ref. [38]. Copyright © (2007) Elsevier Masson SAS.

Both complexes are narrow gap semiconductors with σ_{RT} = 0.1 and 15 S cm^{-1} and E_a = 0.055 and 0.03 eV, respectively. The increase of electric conductivity from Fe to Co correlates well with the reduction of the unit cell volume and can be explained by the difference in size of the transition metal cations.

f.) TTF-based radical cation salts with other carborane anions

Examples of tetrathiafulvalene based radical cation salts with carboranes other than transition metal bis(dicarbollide) complexes are rare. The TTF salt with dodecamethyl-carbadodecaborane $(TTF)[MeCB_{11}Me_{11}]$ (**34**) was prepared by oxidation of tetrathiafulvalene with the corresponding carboranyl radical followed by crystallization from dichloromethane/hexane (Scheme 10) [46].



Scheme 10

The single crystal X-ray study of salt **34** demonstrated that the TTF radical cations are isolated from each other by the carborane anions disrupting the formation of the donor stacks suitable for electrical conduction (Figure 14) [46].

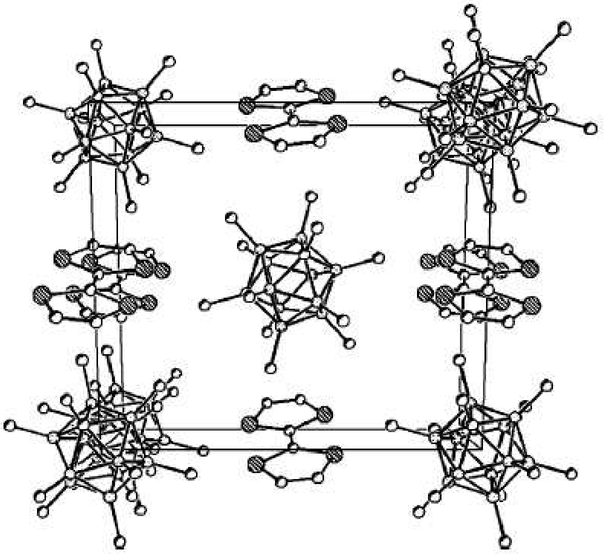
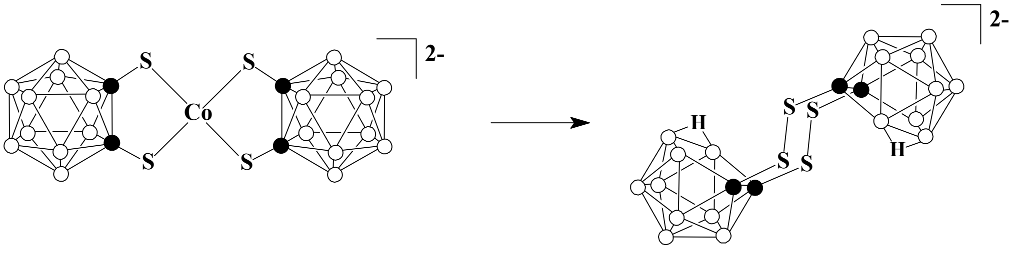


Figure 14. The crystal packing of (TTF)[$MeCB_{11}Me_{11}$] (**34**). Reproduced with permission from [46]. Copyright © (2007) American Chemical Society.

An attempt to prepare tetrathiafulvalenium based salts with bis(*ortho*-carborane-1,2-ditiolato)cobalt(2-) anion $[Co(1,2\text{-}S_2C_2B_{10}H_{10})_2]^{2-}$ by electrochemical oxidation of BEDT-TTF and TMTTF in the presence of $(Me_4N)_2[Co(1,2\text{-}S_2C_2B_{10}H_{10})_2]$ unexpectedly resulted in demetallation of the bis(dithiolate) complex accompanied by partial degradation of the *closo*-carborane cage to the *nido*-carborane one and oxidation of dithiolate to cyclic disulfide (Scheme 11) [47].



Scheme 11

In the result, two new radical cation salts (BEDT-TTF)$_2$[anti-7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate)] (**35**) and (TMTTF)$_2$[anti-7,7′:8,8′-bis(dithio)bis(7,8-dicarba-undecaborate)] (**36**) were obtained. In the salt **35** the BEDT-TTF radical cations form stacks along the *a* axis. The stacks are irregular and consist of dimer pairs that are shifted along the short molecular axis. The distance between the BEDT-TTF planes in the dimer pairs is 3.66 Å. The shortened intermolecular S···S distances (3.50 Å) were found in the dimer pairs, whereas the the S···S distances between the dimers are 3.46 - 3.64 Å. Short interstack S···S contacts (3.54 -

3.61 Å) were also found between the radical cations from neighbor stacks (Figure 15). The salt **35** is semiconductor with room temperature conductivity $\sigma_{RT} = 10^{-3}$ S cm^{-1} and $E_a = 0.19$ eV. Structure of the salt **36** contains the TMTTF dimers which do not form stacks. The interplanar distances in the TMTTF dimer pairs are 3.40 Å (Figure 15). The salt 26 is dielectric with $\sigma_{RT} \sim 10^{-3}$ S cm^{-1} [47].

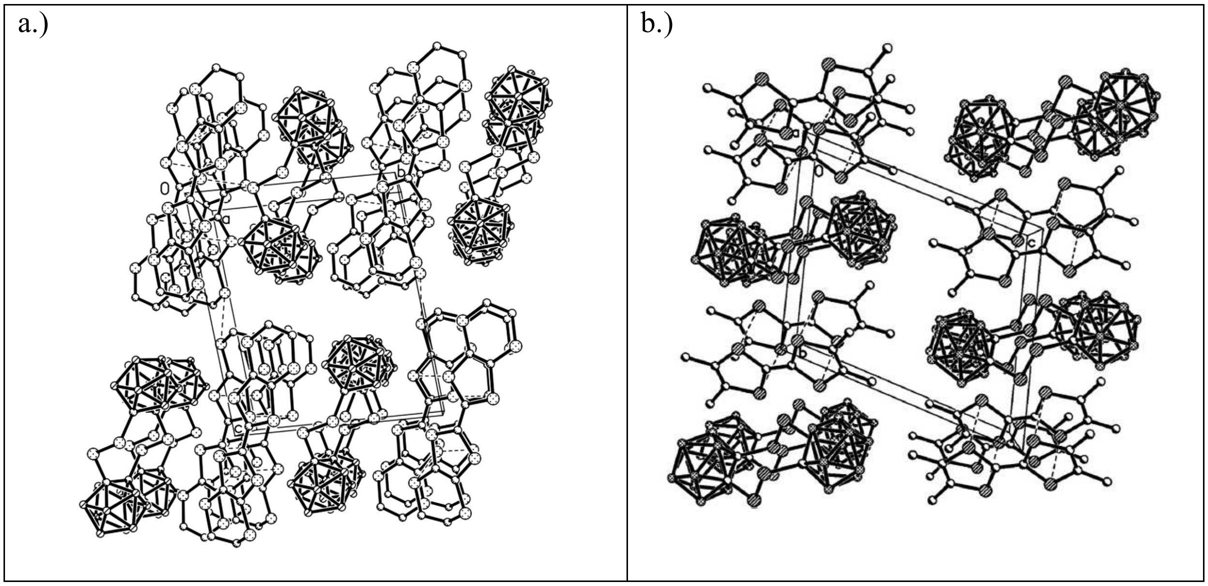


Figure 15. The crystal packing of (a) (BEDT-TTF)$_2$[anti-7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate)] (**35**) and (b) (TMTTF)$_2$[anti-7,7′:8,8′-bis(dithio)bis(7,8-dicarba-undecaborate)] (**36**). Reproduced with permission from Ref. [47]. Copyright © (2013) Elsevier Masson SAS.

4. Conclusions

The radical cation salts based on derivatives of tetrathiafulvalene and transition metal bis(dicarbollides) are of considerable interest for the development of new molecular conducting materials. A number of patterns in the structure and electrical conductivity of these compounds were revealed. It was found that electrical conductivity in the series (BEDT-TTF)$_2$[3,3'-M(1,2-$C_2B_9H_{11}$)$_2$] and (TMTSF)$_2$[3,3'-M(1,2-$C_2B_9H_{11}$)$_2$] increases with the decrease of the metal ion radius. In some cases the conformation of bis (dicarbollide) anion may have a significant impact on the formation of the anion sublattice and, as a consequence, on the packaging of the donor molecules in the crystal. Favorable for the formation of a layered structure conformation of anion can be stabilized by the presence of various substituents in the neighbor to the metal atom belt of the dicarbollide ligand due to additional interactions between the ligands. A regular change of structural parameters and electrical conductivity was revealed in the series of radical-cation salts containing halogenated cobalt bis(dicarbollide) (BEDT-TTF)$_2$(8,8’-X$_2$-3,3’-Co(1,2-C$_2$B$_9$H$_{10}$)$_2$] and (BMDT-TTF)$_4$(8,8’-X$_2$-3,3’-Co(1,2-C$_2$B$_9$H$_{10}$)$_2$] (X = Cl, Br, I). The highest electrical conductivity was found in the most dense packed salts with the chloro-substituted cobalt bis(dicarbollide) anion. On the other hand, the introduction of small substituents, such as hydroxy group, does not produce conformer stabilization. The similar results were obtained with substituents in the second to the metal atom belt of the dicarbollide ligand. However, the increase of anion size must lead to an increase in the anion sublattice and, consequently, to an increase in the cation sublattice promoting the formation of conductive layers and stacks cation radicals. Therefore, of particular interest are the synthesis of radical cation salts with transition metal bis(dicarbollide) ligands containing substituents at different positions of the metallacarborane cage at the same time: substituents in the neighbor to the metal atom belt of the dicarbollide ligand should produce stable conformers and substituents in the second belt should increase effectively the anion size. The future work will be directed on synthesis and study of the radical cation salts with such highly substituted transition metal bis(dicarbollide) anions.

Acknowledgements

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Tetrathiafulvalene-based radical cation salts with transition metal bis(dicarbollide) anions

**Vladimir I. Bregadze[a], Oleg A. Dyachenko[b], Olga N. Kazheva[b],
Andrey V. Kravchenko[c], Igor B. Sivaev[a], Vladimir A. Starodub[d]**

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilov Str. 28, 119991 Moscow, Russia*
[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Semenov Av. 1, 142432, Chernogolovka, Moscow Region, Russia*
[c] *V. N. Karazin Kharkiv National University, Department of Chemistry,
Svoboda Sq. 4, 61077, Kharkiv, Ukraine*
[d] *Institut Chemii Uniwersyteta Jana Kochanowskiego,
ul. Świętokrzyska 15 G, 25-406 Kielce, Polska*