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First molecular conductors of BPDT-TTF with metallacarborane anions: (BPDT-TTF)[3,3′-Cr(1,2-$C_2B_9H_{11}$)$_2$] and (BPDT-TTF)[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] – Synthesis, structure, properties☆

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ABSTRACT

The first molecular conductors based on bis(1,3-propylenedithio)tetrathiafulvalene and transition metal bis(dicarbollides) (BPDT-TTF)[3,3′-Cr(1,2-$C_2B_9H_{11}$)$_2$] (**1**) and (BPDT-TTF)[3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$] (**2**) were synthesized and their crystal structures were determined by X-ray analysis. The electric conductivity measurements revealed that these compounds are semiconductors at room temperature.

1. Introduction

Tetrathiafulvalene-based molecular conductors have remarkably attracted the interest of material scientists for more than 40 years since the pioneering work of Ferraris et al. [1], where the tetrathiafulvalene (TTF) organic donor was combined with the tetracyanoquinodimethane (TCNQ) organic acceptor, yielding the charge transfer complex (TTF)(TCNQ). The new compound revealed unique conducting properties comparable to those of classical metals, which have never been observed before in a purely organic material. Tetrathiafulvalene-based radical-cation salts represent a wide class of organic molecular compounds, interesting as conducting, superconducting, magnetic and hybrid materials. Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has been shown to be the most successful donor, affording the largest number of two-dimensional (2D) conducting materials, ranging from insulators and semiconductors to the majority of the known molecular superconductors [2].

Electronic properties of tetrathiafulvalene-based radical-cation salts are essentially determined by packing pattern of their donor molecules, which in turn, depends on counterions. Therefore, inorganic counterions play a crucial role in physical properties of TTF-based materials and their variation is one of the main approaches to modify physical properties of molecular conducting materials. Organometallic chemistry provides a wide choice of

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☆ We have the pleasure to dedicate this paper to Professor Irina Beletskaya on the occasion of her 85th birthday in recognition of her outstanding contribution to organometallic chemistry.

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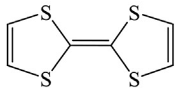
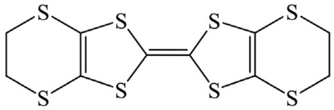
metal complexes of diverse sizes and charges that can be used as charge compensating counterions. The bis(1,2-dicarbollide) complexes of transition metals $[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_2]^-$ demonstrate extraordinary stability due to the delocalized cluster bonding between the transition metal and the ligand orbitals and can be easily modified by substitution of hydrogen atoms at the carbon and boron atoms of the dicarbollide ligands for various non-hydrogen atoms and functional groups [3,4]. It prompted us undertake systematic study of effect of transition metals bis(1,2-dicarbollides) and their derivatives on the structure and electrical conductivity of their TTF-based radical-cation salts. In the frameworks of this study a series of the TTF, BEDT-TTF, BMDT-TTF, TMTTF and TMTSF salts with various bis(1,2-dicarbollide) anions have been studied [5–7].


TTF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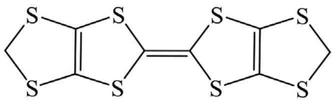
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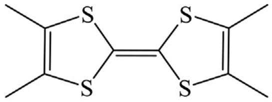
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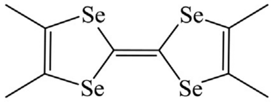
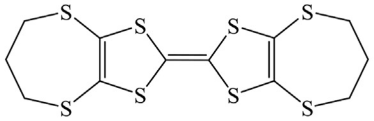

TMTSF


BPDT-TTF

Unlike the TTF and BEDT-TTF radical-cation salts, represented by thousands of compounds, molecular conductors based on bis(1,3-propylenedithio)tetrathiafulvalene (BPDT-TTF) donor are much less studied and form a small group comprising less than twenty compounds. After the synthesis of the first BPDT-TTF-based radical-cation salt $(\text{BPDT-TTF})_3[PF_6]_2$ [8], a series of molecular conductors with linear trihalide anions $(\text{BPDT-TTF})_2ICl_2$ [9,10], $(\text{BPDT-TTF})_2IBr_2$ [11], $(\text{BPDT-TTF})_2I_3$ [12] and transition metal halide complexes $(\text{BPDT-TTF})_3[InI_4]_2$ [13], $(\text{BPDT-TTF})[HgBr_3]$ [14], $(\text{BPDT-TTF})_4[Hg_2Br_6][HgBr_3]$ [15], $(\text{BPDT-TTF})_2[AuBr_2]$ [16], $(\text{BPDT-TTF})_2[Mo_6Cl_{14}]$ [17], as well as salts with polyoxametalate cluster anion $(\text{BPDT-TTF})_2[W_6O_{19}]$ [18] and square planar nickel complex anion $(\text{BPDT-TTF})[\text{Ni(dmit)}_2]_2$ [19] were synthesized. The preparation of halogen-bonded supramolecular networks with the BPDT-TTF^{+} radical-cations located in the network's channels has been reported as well [20,21]. As revealed analysis of the literature data, the conductivity of the BPDT-TTF salts varies in a wide range from semiconducting to metallic. It motivated us to extend our systematic study of effect of transition metal bis(dicarbollide) anions on structure and conductivity of TTF-based radical-cation salts by including here BPDT-TTF radical-cation salts.

In this paper we describe synthesis and properties of the BPDT-TTF^{+} radical-cation salts with metallacarborane anions $(\text{BPDT-TTF})[3,3'\text{-Cr}(1,2\text{-}C_2B_9H_{11})_2]$ (**1**) and $(\text{BPDT-TTF})[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ (**2**).

2. Results and discussion

Single crystals of the 1:1 radical-cation salts $(\text{BPDT-TTF})[3,3'\text{-Cr}(1,2\text{-}C_2B_9H_{11})_2]$ (**1**) and $(\text{BPDT-TTF})[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ (**2**) were prepared by electrochemical anodic oxidation of BPDT-TTF in the presence of the corresponding transition metal bis(dicarbollides) $(Me_4N)[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_2]$ (M = Cr, Co) in 1,1,2-trichloroethane - acetonitrile mixture (12:1) as a solvent.

The crystal structure of $(\text{BPDT-TTF})[3,3'\text{-Cr}(1,2\text{-}C_2B_9H_{11})_2]$ (**1**) is formed by the BPDT-TTF^{+} radical-cation and the $[3,3'\text{-Cr}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion located in special centrosymmetrical positions (Fig. 1). In the structure of **1** the radical-cations and anions alternate along the *ac* diagonal (Fig. 2). There are no short intermolecular interactions between the radical-cations and the anions.

The BPDT-TTF^{+} radical-cation is not planar and adopts a chair conformation that is typical of the known BPDT-TTF^{+} radical-cation salts [8–17,19]; the maximum displacement of sulfur atom from mean plane drawn through all sulfur atoms is 0.09 Å (atoms S(3) and S(3 A)), the displacements of the terminal carbon atoms C(3), C(4) and C(5) from this plane are equal to 1.40, 1.30 and 1.45 Å, respectively (Fig. 3a).

The Cr-C and Cr-B distances in the $[3,3'\text{-Cr}\,(1,2\text{-}C_2B_9H_{11})_2]^-$ anion are 2.192(2)–2.216(2) and 2.215(2)–2.258(2) Å, respectively. Practical equivalence of Cr-C (2) (2.216 (2) Å) and Cr-B (4) (2.215 (2) Å) distances as well as C (1)-C (2) (1.644 (3) Å) and C (1)-B (4) (1.640 (3) Å) distances indicate disorder of one carbon atom over positions C (2) and B (4) with approximately equal occupancy. The distances from the chromium atom to the C_2B_3 planes are equal 1.69 Å, that is typical of known salts of the chromium bis(dicarbollide) anion [22,23]. The dicarbollide ligands in the anion are mutually rotated by 180°, the C_2B_3 faces of the ligands are parallel by the crystallographic symmetry conditions.

The crystal structure of $(\text{BPDT-TTF})[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ (**2**) is formed by the BPDT-TTF^{+} radical-cation and the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion located in special centrosymmetrical positions (Fig. 3b, 4). The compounds **1** and **2** are not isostructural, their crystalline packages are similar although. In the structure of **2** the radical-cations and anions alternate along the *ab* diagonal (Fig. 4). There are no short intermolecular interactions between the radical-cations and the anions. The structure of **2** differs from the structure of the known 1:1 radical-cation salt $(\text{BEDT-TTF})[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$, where the BEDT-TTF^{+} radical-cations and the $[3,3'\text{-Co}\,(1,2\text{-}C_2B_9H_{11})_2]^-$ anions form layers alternating along the *b* axis [24]. Since the HOMO distribution of the BPDT-TTF molecule is very similar to that of the BEDT-TTF molecule [25] this difference is probably due to the structural features of the BPDT-TTF^{+} cation.

The BPDT-TTF^{+} radical-cation is also not planar and adopts a chair conformation; the maximum displacement of sulfur atom from mean plane drawn through sulfur atoms is only 0.03 Å (atoms S(4) and S(4 A)), whereas the displacements of the terminal carbon atoms C (3), C (4) and C (5) from this plane are much larger than in the structure of **1** and are equal to 1.59, 1.65 and 1.61 Å, respectively (Fig. 3b).

The Co-C and Co-B distances in the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ anion are 2.058(2)–2.064(2) and 2.070(2)–2.086(2) Å, respectively. Nearly equivalent Co–C(1) (2.058 (2) Å), Co–C (2) (2.064 (2) Å), Co–B(4) (2.072 (2) Å) and Co–B(7) (2.070 (2) Å) bond lengths suggest possible disorder of boron and carbon atoms at the

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