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First hybrid radical-cation salts with halogen substituted iron bis(dicarbollide) anions – synthesis, structure, properties

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ABSTRACT

New radical-cation salts based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) were synthesized: $(ET)_2[8,8'\text{-}Br_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**1**) and $(ET)[8,8'\text{-}I_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ (**2**). Their crystal structures were studied by X-ray analysis, electroconducting and magnetic properties were measured in a wide temperature range. Salts (**1**) and (**2**) appeared to be the first radical-cation salts with $[8,8'\text{-}I_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ and $[8,8'\text{-}Br_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ anions, respectively. In the literature $[8,8'\text{-}I_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ and $[8,8'\text{-}Br_2\text{-}3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]^-$ anions are presented for the first time. Salts (**1**) and (**2**) were found to be paramagnetic. Their room temperature conductivities were 2 and $1 \cdot 10^{-6}$ $Ohm^{-1}cm^{-1}$, respectively.

1. Introduction

Controlling structural characteristics which are responsible for peculiarities of physical properties of materials is the main technique of new materials design. In search of new functional materials the selection of suitable building blocks namely molecules with appropriate structural, electronic and functional features are of great importance, since it allows achieving a desired supramolecular architecture. Such molecules are represented by organic π-electron donors - tetrathiafulvalene (TTF), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and their derivatives, generating radical-cation salts with wide range of electroconducting properties, from semiconducting to metallic and even superconducting [1–3].

Electroconductivity of these compounds on one hand depends on cationic sublattice: π-donors have been self-organized in stacks or sheets, where short intermolecular S···S contacts appear and electron transfer takes place. On the other hand the impact of anion sublattice, determining the architecture of radical-cation layer is also substantial. Thus, the choice and variation of anion's structure in radical-cation salts is the main resource of achieving a desired structural organization and physical properties of the crystals.

Functionalized derivatives of metallacarboranes are of increased interest for many aspects of fundamental [4] and applied chemistry [5].

Metallacarboranes derivatives are prospective anions for the synthesis of radical-cation salts due to their peculiarities. The bis(1,2-dicarbollide) complexes of the iron group metals, [*commo*-$3,3'\text{-}M(1,2\text{-}C_2B_9H_{11})_2]^-$ (M = Fe, Co, Ni), possess a high stability due to the delocalized cluster bonding of the metal atom with π orbitals of the dicarbollide ligands [6,7]. The hydrogen atoms in these compounds can easily be substituted by various atoms and groups,

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as well as an introduction of different substituents opens practically unlimited prospective of their modification. Thus, counter ions with a variety of volumes, connectivity, shapes and charges can be prepared [6–9], That provides an important strategy for the molecular design to control molecular assembly in radical-cation salts. Besides, application of magnetic metals in such anions gives the possibility of introduction of an additional functional characteristic, magnetic property, into the electroconductive crystal.

The synthesis and research of radical-cation salts based on TTF, ET and their derivatives has become of interest in around the world [10–15]. However not so many works have been published using metallacarborane anions in radical-cation salts composition [16–19] and mostly of them are so far our studies [20–28].

In this report we describe synthesis, crystal structure, magnetic properties and electrical conductivity of ET salts of 8,8'-dihalogen derivatives of iron bis(dicarbollide) anion $[8,8'\text{-Hal}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]^-$: $(ET)_2[8,8'\text{-Br}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**1**) and $(ET)[8,8'\text{-I}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**2**).

2. Experimental

2.1. Materials and methods

Chemicals were reagent grade and received from standard commercial vendors. The complex $Cs[3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{11})_2]$ was prepared according to the literature procedure [29]. THF was distilled from Na/benzophenone ketyl prior to use. TLC was performed on Kieselgel 60 F245 (Merck) plates. Column chromatography was performed on silica gel 60 0.060–0.200 (Acros Organics). The ^1H, ^{11}B NMR spectra were recorded on Bruker Avance-400 spectrometer. The negative ion electrospray ionization mass spectra were obtained with a micro-OTOF II instrument (Bruker Daltonics) operating in a mass range of m/z 50–3000. Elemental analysis was performed in the Microanalytical laboratory of the A.N. Nesmeyanov Institute of Organoelement Compounds.

2.1.1. Synthesis of $[Me_4N][8,8'\text{-Br}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (3)

N-Bromosuccinimide (0.40 g, 2.25 mmol) was added to a solution of $Cs[3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{11})_2]$ (0.50 g, 1.11 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred for 1.5 h at the room temperature. The solvent was evaporated. The rest was dissolved in 5 mL of acetone, treated with an excess of aqueous solution of Me_4NBr and then was stored in a fridge for a few hours. The precipitate formed was recovered by filtration and purified by column chromatography on silica with a solvent mixture of CH_2Cl_2 and MeCN (10/1 v/v) as eluent. The major fraction was collected and vacuum dried to give 0.56 g (92%, rufous solid) of **3**. The spectral characteristics of the complex **3** perfectly match the literature data [30].

2.1.2. Synthesis of $[Me_4N][8,8'\text{-I}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (4)

N-Iodosuccinimide (0.50 g, 2.22 mmol) was added to a solution of $Cs[3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{11})_2]$ (0.50 g, 1.11 mmol) in anhydrous THF (20 mL). The reaction mixture was stirred for 45 min at the room temperature. The solvent was evaporated. The rest was dissolved in 5 mL of acetone, treated with an excess of aqueous solution of Me_4NBr and was stored in a fridge for a few hours. The precipitate formed was recovered by filtration and purified by column chromatography on silica with a solvent mixture of CH_2Cl_2 and MeCN (10/1 v/v) as eluent. The major fraction was collected and vacuum dried to give 0.70 g (98%, gray-asparagus solid) of **4**. Found (%): C, 14.51; H, 4.93. $C_8H_{32}B_{18}FeI_2N$: requires (%): C, 14.86; H, 4.99. ^1H NMR (acetone-d6, δ, ppm): 58.59 (CH-carborane). ^{11}B NMR (acetone-d6, δ, ppm): 121.8, 25.3, 7.1, −48.4, −337.8, −573.3. HRESIMS: found 573.0790; $C_4H_{20}B_{18}FeI_2$ requires 573.0796.

2.1.3. Synthesis of radical-cation salts

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) (Aldrich) was used as received. $K[8,8'\text{-I}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2B_9H_{10})_2]$ was prepared as previously described [16]. New radical-cation salts $(ET)_2[8,8'\text{-Br}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**1**) and $(ET)[8,8'\text{-I}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**2**) were grown by anodic oxidation of bis(ethylenedithio)tetrathiafulvalene, in the presence of $[Me_4N][8,8'\text{-Hal}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2B_9H_{10})_2]$ (Hal = Br or I, respectively) and 18-crown-6 under argon atmosphere. The crystals were grown by electrochemical crystallization under galvanostatic conditions in standard two-electrode H-cell with platinum electrodes separated by glass frit. The current applied was changed discretely on 0.05–0.10 μA per day from 0.10 to 1.00 μA. The period of crystal growth was 4–5 weeks.

Crystals of **1** were obtained from the $[Me_4N][8,8'\text{-Br}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (8×10^{-3} M) – 18-crown-6 (1.5×10^{-2} M) – ET (2×10^{-3} M) system using 1,1,2-trichloroethane – acetonitrile (5:1) as solvents. Crystals of **2** were obtained from the $[Me_4N][8,8'\text{-I}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (8×10^{-3} M) – 18-crown-6 (1.5×10^{-2} M) – ET (2×10^{-3} M) system using 1,1,2-trichloroethane - acetonitrile (5:1) as a solvent.

2.2. Single-crystal structure determination

X-ray diffraction studies of (**1**), (**2**) salts were carried out with a Bruker APEX-II CCD diffractometer, using graphite monochromated Mo-K_α radiation (φ, ω-scanning). The structures were solved by direct methods followed by Fourier difference syntheses using SHELXS software [31] and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms using SHELXL software [32]. The reflection intensities were corrected for absorption using SADABS program [33]. The hydrogen atoms were fixed in positions of ideal geometry.

Details concerning the crystal data collection and refinement parameters for compounds **1**, **2** are summarized in Table 1. Bond lengths are listed in Tables S1–S2.

2.3. Electric resistivity measurements

The temperature dependence of electric resistivity was measured on single crystals of **1** and polycrystal of **2**, using standard

Table 1
Crystal data and structure refinement for $(ET)_2[8,8'\text{-Br}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**1**) and $(ET)[8,8'\text{-I}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2B_9H_{10})_2]$ (**2**).

Compound	(1)	(2)
Empiric formula	$C_{24}H_{36}B_{18}Br_2FeS_{16}$	$C_{14}H_{28}B_{18}FeI_2S_8$
Formula weight	1247.74	957.07
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.8412(5)	6.932(2)
b (Å)	8.9053(6)	10.972(2)
c (Å)	21.161(1)	11.069(3)
α (°)	82.579(1)	98.228(3)
β (°)	91.012(1)	91.819(4)
γ (°)	67.038(1)	94.546(3)
V (Å^3)	1173.84(14)	829.8(3)
Z	1	1
λ (Å)	0.71073	0.71073
D_{calc} (Mg m^{-3})	1.76	1.91
μ (mm^{-1})	2.762	2.832
Number of reflections collected	9303	8121
Number of independent reflections	5154	4116
Number of reflections with $[F_0 > 4\sigma(F_0)]$	4003	3722
Number of parameters refined	277	196
$(2\theta)_{max}$ (°)	56.62	57.40
R	0.055	0.026

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