

ABSTRACT

Chudak D.M. Conductive radical-cation salts of fulvalenes with complex meta-anions. Qualification scholarly paper: a manuscript.

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Actuality of theme. One of the fundamental tasks of science and technology is the creation of new materials with combined properties. Among such materials, traditionally, one of the important places is occupied by molecular conductors, which are increasingly being widely used.

The ability to have the properties of metals is common among inorganic compounds, and in organic compounds the metallic state is an exceptional phenomenon. There is the electrical conductivity of conjugated and aromatic systems in organic compounds, which is formed by the collectivization of π -electrons within a single molecule. Following Bardin-Cooper-Schriffer's proposed theory of superconductivity in metals, Little suggested in 1964 that superconductivity could occur in the organic chain of a molecule and occur even at room temperature. This idea aroused great interest and led to the search for organic superconductors. The synthesis of organic compounds with metallic conductivity and called "organic metals" was a significant event of the late XX century.

Currently, the main class of molecular conductors are radical-cation salts (RCS) based on organic π -donors, which are of considerable interest due to the diversity of their structural types and the wide range of transport properties. These are quasi-two-dimensional systems that have a layered structure. A characteristic feature of this structure is the presence of conductive radical-cation layers, which alternate with stacks of anions. The cationic and anionic layers are spatially well separated in the crystal, forming two sublattices. The conduction band is formed by the higher occupied molecular orbitals of cation radicals. Anions that act as electron acceptors affect the type of packaging of donor molecules, which depends on the nature of transport properties. As a rule, they are not directly involved in the conduction process. But having their own specific properties (magnetic, photochromic, nonlinear optical and others), can affect the corresponding physical properties of crystals.

The question of the complementarity of organic and inorganic layers is important in the formation of RCS crystals. The difference in the translation parameters of the sublattices can lead to the formation of both proportional and disproportionate structural modulations. Conductors with different structural and physical properties can be obtained with the same donor by varying the composition of the anionic sublattice.

From the point of view of molecular conductor design, bis (dicarbolyde) complexes of transition metals $[3,3'-M(1,2-C_2B_9H_{11})_2]^-$ are very promising, where $M = Fe, Co, Ni$, represent a promising class of compounds for preservation molecular conductors. They have high stability, the ability to change the charge and nature of the metal, as well as modification of the primary bis (dicarbolyde) through a wide targeted introduction to various consumers. Derivatives of bis (dicarbolyde) d-metals have been widely used for liquid extraction and separation of stable and radioactive nuclides. In addition, they are obtained with promising components of ion-selective electrodes, as well as agents for interfacial catalysis.

The thesis is devoted to the research of structure and physical properties of cation - radical salts on the basis of tetrathiafulvalene derivatives with bis (dicarbolyde) anions, which are synthesized by electrochemical method of cation radical generation.

There are a number of works devoted to the study of RCS with diamagnetic dicarbolyde anion Cobalt and its derivatives, in which their structure and conductive properties are analyzed and studied. At the same time, studies with paramagnetic bis (dicarbolydes) of iron have not been successful in electrosynthesis. Therefore, one of the tasks was to improve the conditions of electrochemical synthesis of the leading radical-cation salts of tetrathiafulvalene derivatives in order to obtain the corresponding single-crystal samples.

As a result, we were able for the first time to obtain new single crystals with halogen-substituted bis (dicarbolyde) of Ferrum (III $D_n[8,8'-X_2-3,3'-Fe(1,2-C_2B_9H_{11})_2]$ (where $D = BEDT-TTF$ - bis(ethylenedithio)tetrathiafulvalene, $EOTT$ - 4,5-ethylenedithio-4', 5' - (2-oxatrimethylenedithio) -tetrathiafulvalene, $BPDT-TTF$ - bis (propylenedithio) -tetrathiafulvalene, $X = Cl, Br, I$; $n = 1,2$). Like their structural counterparts, these compounds consist of conductive radical-cation layers having a characteristic β -type packaging and anionic layers. A structural feature of these RCS is the presence in the conductive layer of dimers of the donor molecule, in which there are shortened intermolecular S...S contacts. There are also numerous shortened intermolecular S...S contacts, both in stacks of dimers of the type "face to face" and between them - of the type "side by side". The study of the electrical conductivity of RCS showed that in a number of salts $(BEDT-TTF)_x[8,8'-Hal_2-3,3'-Fe(1,2-C_2B_9H_{11})_2]$ the conductivity of the radical-cation salt decreases with increasing halogen size. 5, 2 and $1 \cdot 10^{-6} \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$, respectively), which is associated with the "loosening" of the structure. Although shortened intermolecular contacts in the anion - radical-cation ($I \cdots S$) system were found in iodine-derived RCS with bis (ethylenedithio) tetrathiafulvalene, this did not increase its electrical conductivity.

The analysis of the obtained RCS in the series $(D)_2[8,8'\text{-Cl}_2\text{-}3,3'\text{-Fe}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ (where $D = \text{BEDT-TTF}, \text{EOTT}, \text{BPDT-TTF}$) showed that with the increase of the radical the conformation of the donor molecule changes from almost planar to the conformation of the "chair". Thus, the packing in the middle of the dimers is compacted, as a result of which the distance between the dimers themselves increases and the structure becomes more fluffy. Specific resistance studies confirm this effect, and in a number of RCS with $\text{BEDT-TTF}, \text{EOTT}, \text{BPDT-TTF}$ - the electrical conductivity decreases (σ_{RT} 0.5, 0.2 and 0.05 $\text{Ohm}^{-1}\cdot\text{cm}^{-1}$, respectively).

The use of a more planar donor, dibenzotetrathiafulvalene (DB-TTF), has resulted in new DB-TTF RCS with Ferrum (III) and Chromium (III) bis(dicarbolides). A characteristic feature of the crystal structures of related compounds is the method of overlapping cation radicals in the stack - the long axes of neighboring molecules are rotated relative to each other by $\sim 30^\circ$. Electrophysical measurements of these salts have shown that these compounds are semiconductors, and the conductivity of the salt $(\text{DB-TTF})_2[3,3'\text{-Cr}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ is approximately 500 times higher than that of its BEDT-TTF counterpart. This is due to the fact that in the structure $(\text{DB-TTF})_2[3,3'\text{-Cr}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ stacks of cation radicals are regular, while $(\text{BEDT-TTF})_2[3,3'\text{-Cr}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ is characterized by dimeric stacks of cation radicals. This, once again, emphasizes the important role of the donor molecule, DB-TTF , in the formation of the conductive layer of the radical-cation salt.

Intensive studies of Bechgaard and Fabre salts have shown a wide range of their properties from dielectric to superconducting, in which metal-dielectric transitions occur at low temperatures. Therefore, we synthesized bovine tetramethyltetrahalcogenofulvalenes with metal-carborane anions. As a result of electrophysical measurements it was found that salts of tetramethyltetrathiafulvalene with $[3,3'\text{-M}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]$ ($M = \text{Fe}, \text{Cr}$) is a dielectric, the conductivity of crystals at room temperature is less than $10^{-10} \text{ Ohm}^{-1}\cdot\text{cm}^{-1}$. The low value of electrical conductivity is consistent with stoichiometry and non-layered salt structure, as well as the angle of inclination of the cation radical in the stack, which achieves a slight degree of overlap of neighboring cation radicals and, accordingly, the orbitals of S atoms of neighboring cation radicals.

In the dissertation work for the first time: (1) the conditions of electrochemical production of leading single crystals of radical-cation salts with tetrathiafulvalene derivatives are optimized. (2) RCS with paramagnetic anions of halogen-substituted iron dicarbolides was synthesized by the method of anodic oxidation of π -electron donors, which allowed to investigate the effect of the magnetic component on the correlation "structure - conductive properties". (3) The influence of the substituent in the anion on the conformation of the dicarbolide ligand and the packing of cation radicals in the conductive layer has been studied. (4) It was found that bulk radicals

in the structure of primary tetrathiafulvalene cause "loosening" of the conductive layer, which, in turn, leads to low conductivity. (5) Electrophysical and magnetic properties were determined for the synthesized single crystals, correlations "structure - conductive properties" were studied.

The practical significance of the results obtained. Conditions for electrochemical synthesis of RCS single crystals have been improved; For the first time, new leading radical-cation salts of tetrathiafulvalene derivatives with metallic carbonic anions having magnetic properties were obtained.

Key words: radical-cation salts, derivatives of tetrathiafulvalene, crystal structure, electroconductivity, magnetic properties, metallacarborane, molecular conductors.