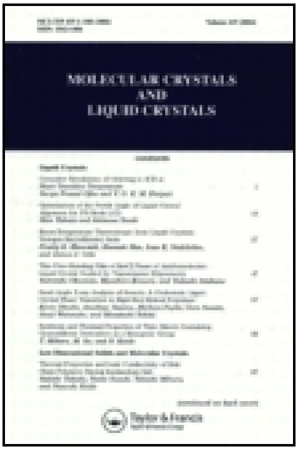

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The Organic Metals Based on a New Hydrogen-Free Fulvalene-C_6S_{12}

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The Organic Metals Based on a New Hydrogen-Free Fulvalene–C_6S_{12}

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Hydrogen-free analogous of the bis-(ethylenedithiolo)-tetrathiafulvalene (ET) C_6S_{8+2n}, n=1, 2 and 3 (C_6S_{10}, C_6S_{12},. C_6S_{14}) were synthesized for the first time using an original method. Thin films of conducting cation-radical salt (CRS) $(C_6S_{12})(ClO_4)_x$ were fabricated using electrochemical method. IR-spectrums and resistance measurements reveal that the CRS is organic metal-like compound which has an unusual transition near 100 K. At this temperature resistance increases about 8 times. Further decrease of temperature down to 77 K leads to decrease of the resistance.

Keywords: Hydrogen-free fulvalene; bis-(ethylenedithiolo)-tetrathiafulvalene; cation-radical salts; organic metals

Progress in the field of organic ("synthetic") metals and superconductors is defined by the possibility to synthesize the novel organic donors capable to production quasi-three-dimensional electronic structures in addition to traditional quasi-two- dimensional ones. In the cation-radical salts (CRS) on the base of bis-(ethylenedithio)-tetrathiafulvalene (ET) and its analogs that is achieved due to creation of reduced intermolecular S…S contacts in the direction perpendicular to the long axis of the molecule [1]. The same is the case for complex isotrithionedithiolates (dmit complexes), in which, as it was noticed in

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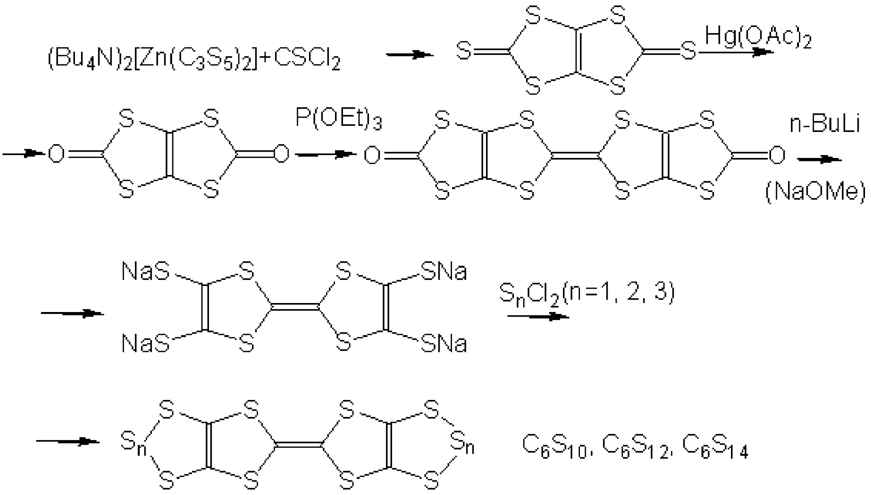
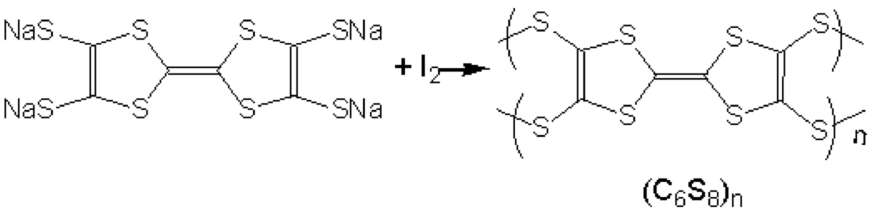
[2], creation of reduced (compared to the sum of van-der-Vaals radii) contacts via the sulphur atoms of thion groups is possible. This allows classifying the above complexes as quasi-three-dimensional conducting systems. Substitution of alkyl radicals in ET molecule by sulfur atoms could favor the establishment of that type of contacts in the direction of the long axis of the molecule also. Synthesis of the sort of hydrogen-free analogs of ET C_6S_{8+2n} (for n = 1 we obtain an analog of bis-(methylenedithio)-tetrathiafulvalene – MT, for n = 2 – an analogue of ET, for n = 3 – an analog bis-(propylenedithio)-tetrathiafulvalene – PT) has been first performed by our original technique presented in schemes 1–2. Synthesis of the resulting CRS $(C_6S_{12})(ClO_4)_x$ has been performed electrochemically.



SCHEME 1



SCHEME 2

EXPERIMENTAL

Tetrabutylammonium i-trithionedithiolatozincate $[(H_9C_4)_4N]_2\ [Zn(dmit)_2]$ has been obtained by the technique described in [3], with carbon disulphide reduction with sodium performed at –10 C temperature.

Production of [1,3]-dithiolo[4,5-d]-1,3-dithiol-2,5-dithion (**I**), [1,3]-dithiolo[4,5-d]-1,3-dithiol-2,5-dion (**II**) and 5-(5-oxo[1,3]dithiolo[4,5-d]-1,3-dithiol-2-yliden)[1,3]dithiolo[4,5-d]-1,3-dithiol-2-on (**III**) has followed the techniques of [4] paper. A high yield of the synthesis has been achieved for all the compounds: (**I**) – 92% (46% in [3]); for (**II**) – 60% % (33% in [3]) and for (**III**) – 80.5% (76%) in [3]).

Dichloromonosulfan and dichlorodisulfan "Aldrich" produced have been purified by methods recommended by G. Brauer manual [5], for the synthesis of dichlorotrisulfan the following technique was used [6].

In order to obtain $(MS)_4$TTF (M – Li, Na) salts, reactions of (**III**) dion with a solution of n-butyl lithium in hexane or with sodium methylate solution in methanol have been used.

$C_6\ S_{10}^{\cdot}\frac{2}{3}(C_9H_{18}O)$. 1.3 ml of n-butyl lithium solution (concentration 1.6 mol/l) was added to 200.8 mg of (**III**) dion in the form of suspension in 10 ml of tetrahydrofuran. After 15 minutes long mixing it yields a dark-brownish solution of $(LiS)_4$TTF salt. To the obtained solution dichloromonosulfan (0.07 mol in 10 ml of acetonitrile) was added and mixed for 3 hours. The obtained dark-brownish precipitate was filtered and washed by acetonitrile, acetone, water, again by acetone and vacuum-dried. Yield of the final product has reached 86%. Found, %: C – 29.57, H – 2.56, S – 65.69. $C_{12}H_{12}O_{0.67}S_{10}$. Calculated, %: C – 29.56, H – 2.48, S – 65.77, which corresponds to $C_6\ S_{10}^{\cdot}\ \frac{2}{3}(C_9H_{18}O)$ formula.

$C_6\ S_{12}^{\cdot}\ \frac{2}{3}(C_9H_{18}O)$. Produced by the same technique, with $(LiS)_4$TTF solution adding to a solution of dichlorodisulfan. Yield 88%. Found, %: C – 25.55, H – 2.12, S – 69.68. $C_{12}H_{12}O_{0.67}S_{12}$. Calculated, %: C – 26.12, H – 2.19, S – 69.75, which corresponds to $C_6\ S_{12}^{\cdot}\ \frac{2}{3}(C_9H_{18}O)$ formula.

$C_6\ S_{14}^{\cdot}\frac{1}{2}(C_9H_{18}O)$. Produced by the same technique, with $(LiS)_4$TTF solution adding to a solution of dichlorotrisulfan in CCl_4. Yield 91%. Found, %: C – 20.48, H – 1.56, S – 75.47. $C_{12}H_{12}O_{0.67}S_{12}$. Calculated, %: C – 21.30, H – 1.53, S – 75.82, which corresponds to $C_6\ S_{14}^{\cdot}\ \frac{1}{2}$ $(C_9H_{18}O)$ formula.

$C_6\ S_{10}^{\cdot}[(H_3CO)_2CO]$. Suspension of 0.89 g (2.31 mmol) of dion (**III**) in 50 ml of methanol was added to 9.26 mmol of methanol solution of sodium methylate and mixed until the dark-brownish transparent solution of $(NaS)_4$TTF salts was produced (about 5 hours). The solution was in vacuum evaporated and a dry product is obtained. This product was dissolved in acetonitrile, added to the equivalent amount of acetonitrile solution of dichloromonosulfan and mixed for 4 hours. The obtained sediment was filtered, washed by acetonitrile, acetone, water, acetone and in vacuum dried. Yield : 83%. Found, %: C – 22.39, H – 1.25, S – 66.42. $C_9H_6O_3S_{10}$. Calculated, %: C – 22.21, H – 1.27, S – 66.38, which corresponds to $C_6\ S^{\cdot}_{10}[(H_3CO)_2CO]$ formula.

$C_6\ S^{\cdot}_{12}[(H_3CO)_2CO]$. Produced by the same technique, yield 87%. Found, %: C – 19.76, H – 1.11, S – 70.35. $C_9H_6O_3S_{12}$. Calculated, %: C – 19.47, H – 1.09, S – 70.86, which corresponds to $C_6\ S^{\cdot}_{12}[(H_3CO)_2CO]$ formula.

$C_6\ S^{\cdot}_{14}[(H_3CO)_2CO]$. Produced by the same technique, yield 86%. Found, %: C – 17.46, H – 1.01, S – 73.16. $C_9H_6O_3S_{14}$. Calculated, %: C – 17.54, H – 0.96, S – 73.23, which corresponds to $C_6\ S^{\cdot}_{14}[(H_3CO)_2CO]$ formula.

The cation-radical salt $(C_6S_{12})(ClO_4)_x$ was produced electrochemically in galvanostatic regime. Hydrogen-free ET analog $C_6\ S^{\cdot}_{12}\tfrac{2}{3}\,(C_9H_{18}O)$ was dissolved in the mixture CS_2– DMF (30% DMF), a solution concentration $2\cdot 10^{-3}$ mol/l. As the background electrolyte perchlorate of tetrabutylammonium has been chosen, with 10^{-2} mol/l concentration. An electric

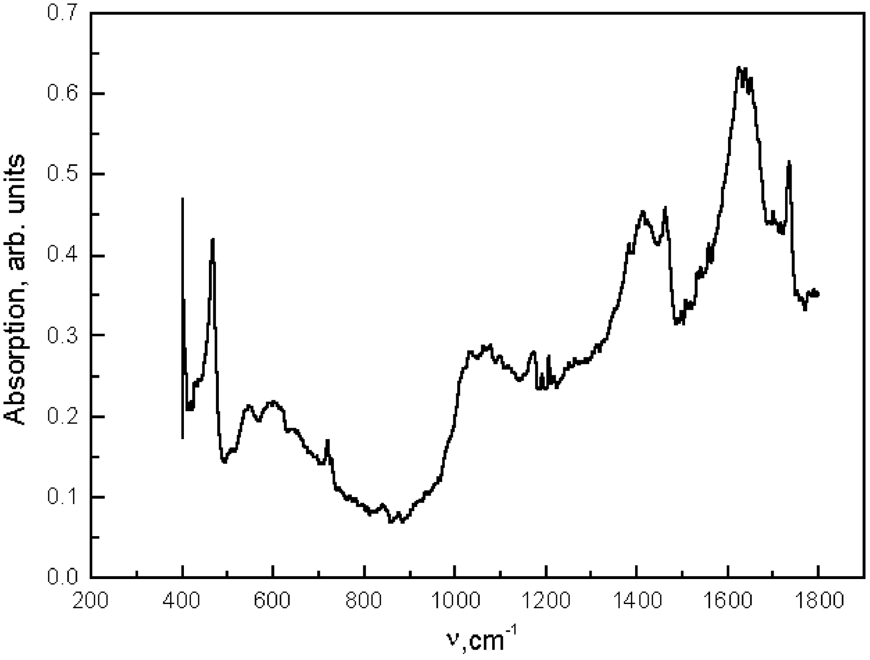


FIGURE 1 IR-spectrum of the CRS (C_6S_{12}) $(ClO_4)_x$.

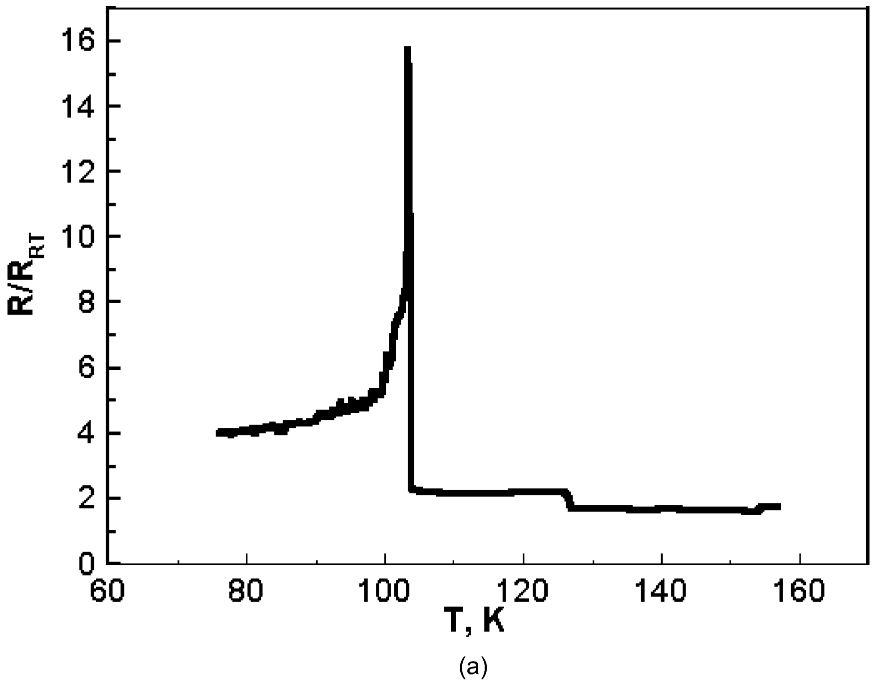


FIGURE 2 Temperature variation of the resistance upon decrease (a) and increase (b) of temperature.

current was fixed at 1 μA during the synthesis. After the 30-day synthesis, dense thin films of CRS have been obtained on an electrodes surface.

IR absorption spectra of the samples pelleted with KBr were measured by Specord 75 IR in the range of 400 – 4000 cm^{-1}. Figure 1 presents IR the spectrum of electrosynthesized CRS $(C_6S_{12})(ClO_4)_x$.

Measurement of the temperature dependence of electric conductivity of this CRS has required the special experimental technique. A fragment of a film-covered electrode was cut, part of the film removed to produce two segments of CRS film separated by platinum layer (see the scheme in Fig. 3). Using indium contacts, electric resistivity of thus produced complex was measured in the temperature range 300–76 K. Figure 2 presents obtained temperature dependences of resistivity at coating and reheating.

RESULTS AND DISCUSSION

Our first developed technique has allowed to synthesize hydrogen-free analogues of bis-(methylenedithio)-tetrathiafulvalene – C_6S_{10}, bis-

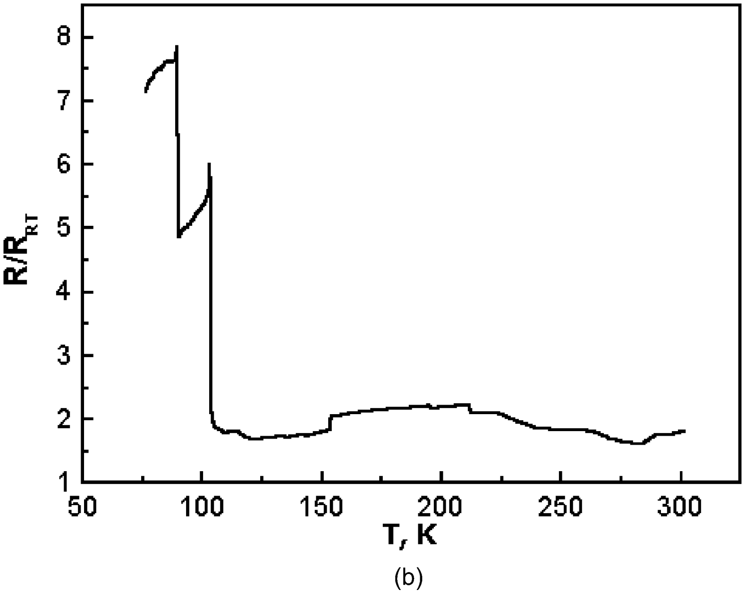


FIGURE 2 (Continued).

(ethylenedithio)-tetrathiafulvalene – C_6S_{12} and bis-(propylenedithio)-tetrathiafulvalene – C_6S_{14}. Synthesized fulvalenes include the molecules of by-products – nonanone-5 when n-butyl lithium was used in the synthesis and dimethyl carbonate when sodium methylate was used. The composition of the produced fulvalenes was testified by the elemental analysis and IR-spectroscopy: in the fulvalene molecules all $C - S$ bonds are weakly polar, as a result, in the IR spectra of studied samples the most intensive bands are related to the vibrations of the bonds of nonanon-5 molecules and dimethyl carbonate, their positions nearly exactly coinsiding with those given in the Atlas of Spectral lines [7]. Meanwhile, in the IR spectrum of $(C_6S_{12})(ClO_4)_x$ CRS strong and broad lines are observed (Fig. 1), which are characteristic for the conducting organic materials.

Such peculiarities are known [8] to the electron-phonon interaction, i.e., an interaction of electronic excitations with totally symmetrical valent vibrations of the fulvalene molecule. Beginning of the continuous absorption in the range of 900 cm^{-1} may be related to excitation of electron's from valent band to conductivity band. This one gives an estimation for the forbidden band width: 0.11 eV.

As it is seen from Figure 2, the only weak dependence of electric conductivity on the temperature above 102 K (up to room temperature)

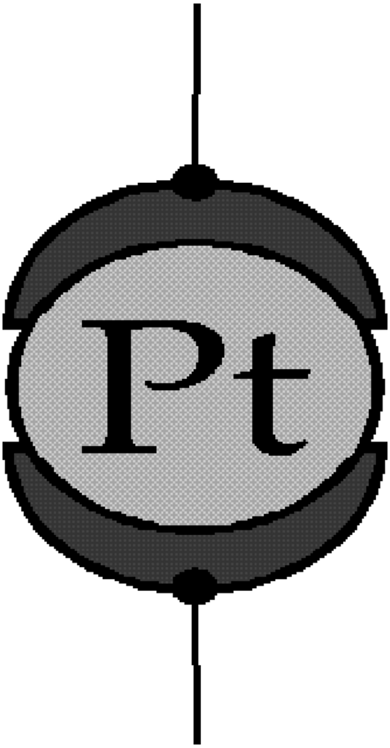


FIGURE 3 Schematic presentation of geometry of resistive measurements.

exists. Below this point an abrupt growth about 8 times of the resistance occurs. the further cooling causes an essential decrease down to 76 K. Reheating of the sample yields the qualitatively similar temperature dependences.

An observed temperature behavior of electric conductivity is quite unusual and may be related to the phase transition at 102 K. Repeated thermocycling reproduces this peculiarity, testifying the validity of the above assumption. For clear understanding of the nature of this transition and of the behavior of $(C_6S_{12})(ClO_4)_x$ conductivity at lower temperatures, further investigations are required.

So, this method is firstly suggested to synthesize hydrogen-free analogues of fulvalenes of the general formula C_6S_{8+2n}, the CRS of possibly 3-d electronic composition. The technique has been tested in a series of successful experiments. as the best conducting material among the obtained compounds a salt $(C_6S_{12})(ClO_4)_x$ retains in a metallic state down to at least 76 K, which proves good prospects of the new fulvalenes in the field of synthesis of novel organic conductors.

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