ESR study of paramagnetic derivatives of sterically hindered di-*o*-quinone with the tetrathiafulvalene bridge

V. A. Kuropatov, S. V. Klementieva, A. I. Poddel´sky, V. K. Cherkasov, and G. A. Abakumov*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831) 462 7497. E-mail: cherkasov@iomc.ras.ru

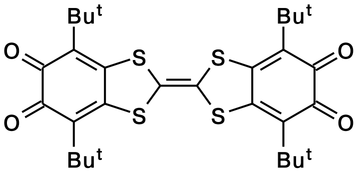
The paramagnetic derivatives of 4,4´,7,7´-tetra-*tert*-butyl-2,2´-bis-1,3-benzodithiol-5,5´,6,6´-tetraone (**1**), *viz*., radical anion salts of the alkali metals (Li, Na, K) and cobaltocenium cations, chelated mono-*o*-semiquinone complexes with different metal fragments (Tl, $TlMe_2$, $SnPh_3$, $Mn(CO)_4$, $Mn(PPh_3)(CO)_3$), a number of copper(I) complexes with sterically hindered phosphines as well as binuclear heterometallic derivatives of triphenylantimony(V) *o*-semiquinone-catecholate with the analogous paramagnetic centers, were studied by ESR spectroscopy. The reaction of di-*o*-quinone **1** with sodium amalgam resulted in the formation of all reduced forms including quinone-semiquinone, disemiquinone, semiquinone-catecholate, and dicatecholate. A radical cation with the unpaired electron localized on the tetrathiafulvalene (TTF) fragment, which resulted from the oxidation of di-*o*-quinone **1**, was detected by ESR spectroscopy.

Key words: 4,4´,7,7´-tetra-*tert*-butyl-2,2´-bis-1,3-benzodithiolidene-5,5´,6,6´-tetraone, tetrathiafulvalene, ESR spectroscopy, metal *o*-semiquinone and catecholate complexes.

Search for the methods for the design of molecular electronic devices remains one of the main trends in the modern materials science.[1—3] The development of approaches to the synthesis of new polyfunctional compounds exhibiting electrical, magnetic, and photoactive properties is topical and interesting. Based on these compounds, it is possible to design new materials, *e.g.*, electro- and photoactive molecular magnetic materials.[4—9]

The coordination and organometallic compounds with the redox-active ligands[10] (primarily, *o*-quinones and their *N*-heteroanalogs) are promising for the design of such materials. *o*-Quinones can form radical anion salts, as well as chelated semiquinone and catecholate complexes with all transition and nontransition metals.[11—14] Using di-*o*-quinones, one can prepare bis- and polyderivatives with the di-*o*-quinone ligand (in one of its reduced forms) as the spacer between two metal centers. To date, a variety of mono- and binuclear metal complexes based on di-*o*-quinones with different bridges between the ligand centers has been studied.[15—20] However, in all known examples, the bridge is not redox-active. The introduction of a redox-active spacer, which can also undergo a reversible oxidation, into the di-*o*-quinone molecule offers additional opportunities for control of the channel connecting the metal centers. The tetrathiafulvalene fragment (TTF) exhibits precisely these properties, *viz*., it can be oxidized reversibly to the radical cation and dication.[21] Since the discovery of the charge-transfer complex TTF•TCNQ[22] (TCNQ is 4,4´,7,7´-tetracyano-*p*-quinodimethane) possessing electrical conductivity, TTF and its analogs are widely used as building blocks in the design of organic conductors and superconductors.[23,24] Therefore, combining redox-active fragments of different nature in one molecule offers prospects for the design of multispin systems with controllable exchange, molecular ferromagnetics, photoswitchable materials, and other molecular devices.

Recently,[25] in search for approaches to the design of such systems, we have synthesized di-*o*-quinone **1** containing two sterically hindered *o*-quinone fragments covalently bound to the TTF spacer and capable of chelate binding to various metal centers. In the present work we studied a number of paramagnetic metal complexes with ligand **1** and its radical cations by ESR spectroscopy.



1

One-electron reduction of **1** with alkali metals and cobaltocene results in radical anion salts **2**—**5** whose ESR spectral parameters are given in Table 1. Since there are no protons and other magnetic nuclei in the quinone rings

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1652—1660, September, 2010.

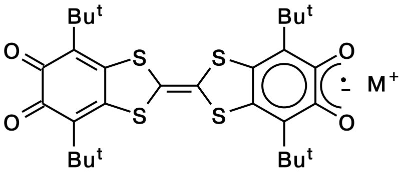
Table 1. The parameters of the isotropic ESR spectra of the paramagnetic derivatives of di-o-quinone **1** in THF at 290 K

Complex*	g_i	A_i(M)	$A_i(^{31}P)$
		mT	
Q-TTF-SQLi (**2**)	2.0056	0.050 (^{7}Li)	—
Q-TTF-SQNa (**3**)	2.0062	0.037 (^{23}Na)	—
Q-TTF-SQK (**4**)	2.0063	—	—
Q-TTF-SQCoCp$_2$ (**5**)	2.0052	—	—
Na$_2$Cat-TTF-SQNa (**8**)	2.0068	0.033 (^{23}Na)	—
Q-TTF-SQTl (**9**)	1.9998	5.24 (^{203}Tl, ^{205}Tl)	—
Q-TTF-SQTlMe$_2$ (**10**)	2.0037	2.84 (^{203}Tl, ^{205}Tl)	—
Q-TTF-SQSnPh$_3$ (**11**)	2.0048	0.86 (^{117}Sn), 0.89 (^{119}Sn)	—
Q-TTF-SQCu(PPh$_3$)$_2$ (**12**)	2.0070	1.01 (^{63}Cu), 1.11 (^{65}Cu)	1.65
Q-TTF-SQCu(dppph) (**13**)	2.0069	1.28 (^{63}Cu), 1.43 (^{65}Cu)	2.04
Q-TTF-SQCu(dppfc) (**14**)	2.0073	1.09 (^{63}Cu), 1.20 (^{65}Cu)	1.87
Q-TTF-SQCuPBu$^t_2$C$_6$H$_4$Ph-*o* (**15**)	2.0063	0.22 (^{63}Cu, ^{65}Cu)	0.13
Ph$_3$PCat-TTF-SQCu(PPh$_3$)$_2$ (**16**)	2.0065	0.91 (^{63}Cu), 1.00 (^{65}Cu)	1.48
Q-TTF-SQMn(CO)$_4$ (**18**)	2.0049	0.36 (^{55}Mn)	—
Q-TTF-SQMn(CO)$_3$(PPh$_3$) (**19**)	2.0032	0.88 (^{55}Mn)	3.15
Ph$_3$SbCat-TTF-SQLi (**21**)	2.0050	0.047 (^{7}Li)	—
Ph$_3$SbCat-TTF-SQNa (**22**)	2.0051	0.034 (^{23}Na)	—
Ph$_3$SbCat-TTF-SQTl (**23**)	2.0003	4.17 (^{203}Tl, ^{205}Tl)	—
Ph$_3$SbCat-TTF-SQCu(PPh$_3$)$_2$ (**24**)	2.0054	0.88 (^{63}Cu), 0.98 (^{65}Cu)	1.43
Ph$_3$SbCat-TTF-SQMn(CO)$_4$ (**25**)	2.0060	0.22 (^{55}Mn)	—
Ph$_3$SbCat-TTF-SQMn(CO)$_3$(PPh$_3$) (**26**)	2.0044	0.64 (^{55}Mn)	2.60
Ph$_3$SbCat-TTF-SQSnPh$_3$ (**27**)	2.0065	0.48 (^{117}Sn, ^{119}Sn)	—
Ph$_3$SbCat-TTF$^{\cdot+}$-CatSbPh$_3$ (**29**)	2.0081	—	—
[Ph$_3$SbCat-TTF$^{\cdot+}$-CatSbPh$_3$][TCNQ$^{\cdot-}$]** (**30**)	2.0086	—	—

* dppph is bis(diphenylphosphino)-*o*-phenylene; dppfc is bis(diphenylphosphino)ferrocene.

** $g(\text{TCNQ}^{\cdot-}) = 2.0040$, $A(4\text{ H}) = 0.042$ mT, $A(4\ ^{14}\text{N}) = 0.145$ mT.

and TTF fragment of the molecule of **1**, except for the ^{13}C and ^{33}S isotopes whose content is extremely low (1.108% and 0.74%, respectively), the ESR spectra display the hyperfine coupling (HFC) only with the nuclei of the magnetic isotopes of the corresponding metals. For example, the ESR spectra of complexes **2** and **3** are quartets caused by the HFC of the unpaired electron with the magnetic nuclei ^{7}Li (92.57%, $I = 3/2$, $\mu_N = 3.2560$) and ^{23}Na (100.0%, $I = 3/2$, $\mu_N = 2.2161$).[26] Lithium semiquinolate can also be obtained upon one-electron reduction of di-*o*-quinone **1** by metallic mercury in the presence of lithium chloride.[27,28] The ESR spectra of the free radical anions of semiquinones **4** and **5** are singlets, because there is no HFC of the unpaired electron with potassium and the magnetic nuclei of the cobaltocenium cation, as in other cases.[18,19,29]



2—5

M = Li (**2**), Na (**3**), K (**4**), Cp$_2$Co (**5**)

Subsequent reduction of **1** with massive metals is complicated due to a low solubility of products. The use of excess sodium amalgam leads to reduction of **1** to the diamagnetic dicatecholate **6**. In addition, each reduced form, *viz.*, quinone-semiquinone (**3**), disemiquinone (**7**), and semiquinone-catecholate (**8**), can be prepared individually by the reaction of **1** with one, two, and three equivalents of sodium amalgam, respectively, or by the addition of the corresponding amount of **1** to dicatecholate **6** (Scheme 1).

Compounds **3** and **6—8** were generated *in situ* to study the ESR spectra of paramagnetic derivatives, as well as these compounds were synthesized on the preparative scale. Complexes **3** and **8** contain an odd number of electrons and the ESR spectra of solutions of these compounds display intense ESR signals as quartets with the characteristic splitting on the magnetic ^{23}Na nuclei (Fig. 1, *a* and *b*). For complex **8**, the HFC constant is somewhat lower (see Table 1). A weak ESR signal observed upon dissolution of complex **7** in THF is the superposition of two quartets with equal intensities (see Fig. 1, *c*), which are due to the

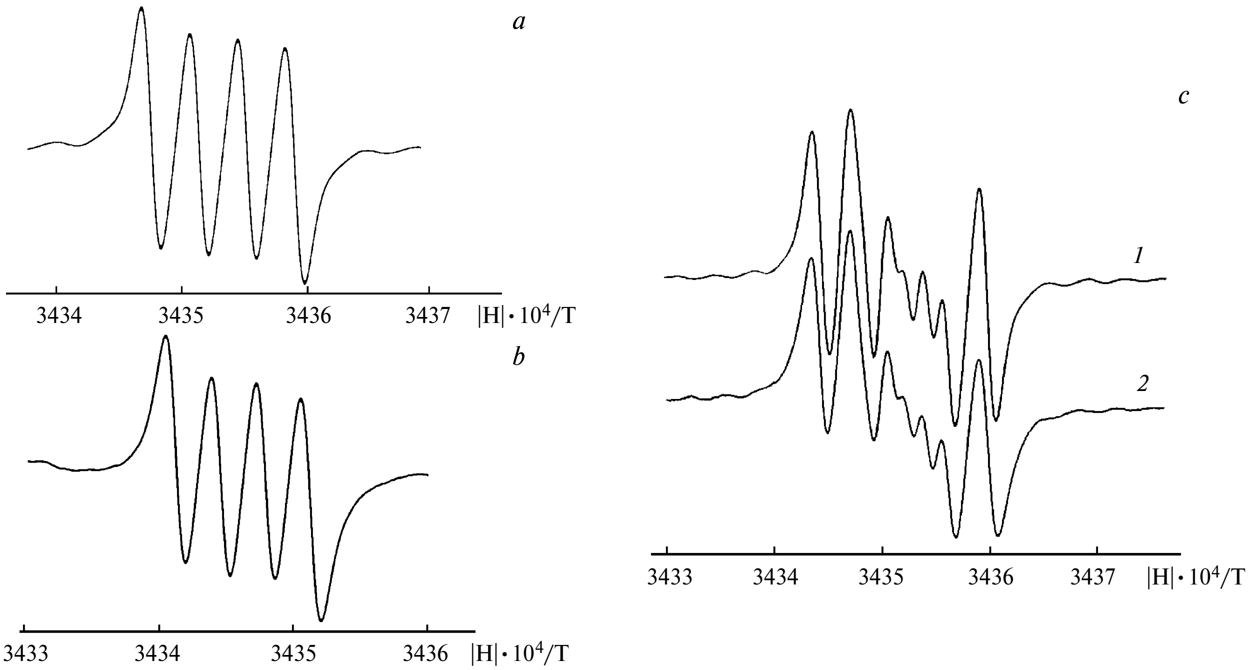
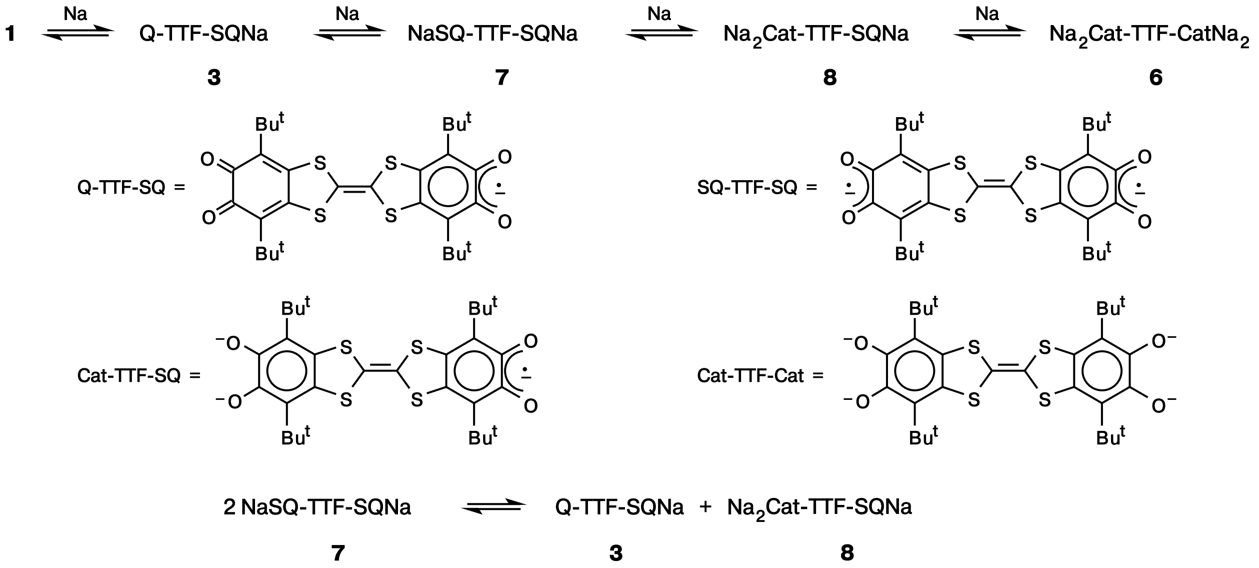


Fig. 1. The ESR spectra of complexes **3** (*a*), **8** (*b*), and **7** (*c*) in THF; spectrum *c* is the superposition of spectra *a* and *b*: *1* is the experimental spectrum (290 K), *2* is the simulated spectrum.

presence of forms **3** and **8** in the solution. Their emergence suggests partial disproportionation of the binuclear complex in the solution (Scheme 1). According to the ESR data, the degree of disproportionation is at most 1%.

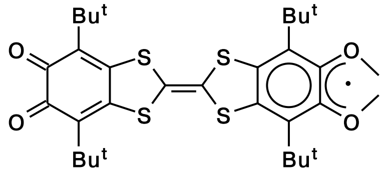
The sodium complexes **3** and **6—8** are stable in inert atmosphere in solution and in the crystalline state; however, they are extremely oxygen- and moisture-sensitive and rapidly oxidized to form the original ligand **1**. The mono- and disemiquinolates **3** and **7**, respectively, isolated by recrystallization from the reaction mixture, are deep-colored fine-crystalline substances, which are almost insoluble in organic solvents, except for THF and MeOH. Solutions of the complexes in THF have deep blue (**3**) and green (**7**) color and are characterized by maxima at 685 and 990 nm, respectively, in the electronic absorption spectra. The stretching frequencies of the carbonyl groups in

Scheme 1



the IR spectrum of complex **3** are lower than those in the spectrum of the starting compound **1** (1599 and 1647 cm^{-1}, respectively).[25] In the IR spectrum of **7**, the corresponding stretching vibrations are observed in the region of 1350—1420 cm^{-1}, which is typical of normal semiquinone complexes.[11—14]

Compounds **8** and **6** corresponding to the higher degree of reduction of **1** are respectively brown and yellow fine-crystalline substances insoluble in organic solvents. The deep-brown precipitate of semiquinone-catecholate **8** makes the solution greenish-brown. The formation of complex **8** occurs immediately upon reduction of a solution of di-o-quinone **1** in THF with three equivalents of sodium amalgam. Subsequent reduction to dicatecholate **6** is possible only when using an excess of sodium amalgam. The C—O stretching vibration bands in the IR spectra of the metal complexes **8** and **6** appear in the regions of 1150—1350 cm^{-1} and 1150—1250 cm^{-1}, respectively, which are typical of the one-and-a-half order bond in the semiquinone fragment and the ordinary bond in the catecholate.[11—14]



9—11

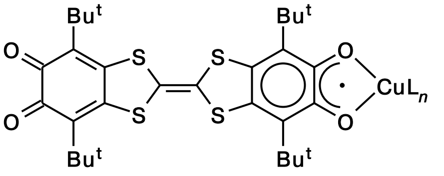
ML$_n$ = Tl (**9**), TlMe$_2$ (**10**), SnPh$_3$ (**11**)

One-electron reduction of **1** with sodium amalgam results in chelated thallium(I) semiquinolate (**9**), as indicated by the appearance of a doublet ESR signal caused by the HFC of the unpaired electron with the magnetic thallium isotopes (^{203}Tl, 29.52%, I = 1/2, μ_N = 1.6222; ^{205}Tl, 70.48%, I = 1/2, μ_N = 1.6382).[26]

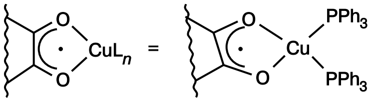
Dimethylthallium semiquinolate **10** was prepared *in situ* by the oxidative reaction of **1** with trimethylthallium at an equimolar reactant ratio. It also has a doublet ESR spectrum; however, the splitting on the magnetic isotopes ^{203,205}Tl is smaller than that in the spectrum of complex **9** (see Table 1). The splittings are typical of the semiquinone complexes of tri- and monovalent thallium, respectively.[17,18]

The ESR spectrum observed upon the reaction of **1** with hexaphenyldistannane is a singlet with satellites due to the HFC of the unpaired electron with the magnetic isotopes of tin (^{117}Sn, 7.75%, I = 1/2, μ_N = 1.000; ^{119}Sn, 8.60%, I = 1/2, μ_N = 1.046)[26]. This signal indicates the formation of triphenyltin semiquinolate **11**.

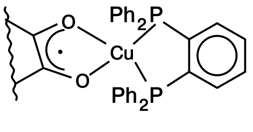
Di-*o*-quinone **1** can dissolve metallic copper in the presence of phospines to form copper semiquinone complexes. The four-coordinate complexes of copper(I) **12—14** with triphenylphosphine, two bidentate phosphines, namely, 1,2-bis(diphenylphosphino)benzene and 1,1´-bis(diphenyldiphosphino)ferrocene, as well as the three-coordinate copper semiquinolate **15** with 2-[di-(*tert*-butyl)-phosphino]biphenyl can also be prepared by the metathesis reaction of sodium or thallium semiquinolate with anhydrous copper(I) chloride in the presence of neutral ligands or by displacement of 3,6-di(*tert*-butyl)-4,5-dimethoxy-*o*-benzoquinone from the corresponding copper(I) complexes.[30—34]



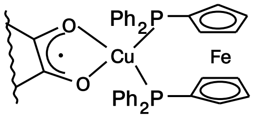
12—15



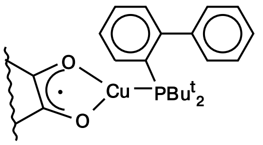
(**12**),



(**13**),



(**14**),



(**15**)

The ESR spectra of complexes **12—14** can be exemplified by the spectrum of complex **13** (Fig. 2, *a*). The observed hyperfine structure (HFS) of the spectrum reveals the HFC of the unpaired electron with the magnetic isotopes of one copper atom (^{63}Cu, 69.09%, I = 3/2, μ_N = 2.2206; ^{65}Cu, 30.91%, I = 3/2, μ_N = 2.3790)[26] and two equivalent ^{31}P phosphorus nuclei (100%, I = 1/2, μ_N = 1.13160)[26] (triplet 1 : 2 : 1). Large values of the constants of HFC with the copper and phosphorus nuclei (see Table 1) suggest a pseudotetrahedral geometry of the coordination sphere.[30—33] The isotropic ESR spectrum of complex **15** is shown in Fig. 2, *b*. The splitting occurs on one ^{31}P nucleus and on the magnetic isotopes of one copper atom. The values of the HFC constants are much smaller than in the spectra of complexes **12—14** (see Table 1) and correspond to the values observed in the ESR spectra of three-coordinate *o*-semiquinone complexes of copper with a planar trigonal geometry.[34]

The reactions of di-*o*-quinone **1** with two equivalents of copper(I) 3,6-di(*tert*-butyl)-4,5-dimetoxy-*o*-benzosemiquinolates containing all the phosphines listed above,

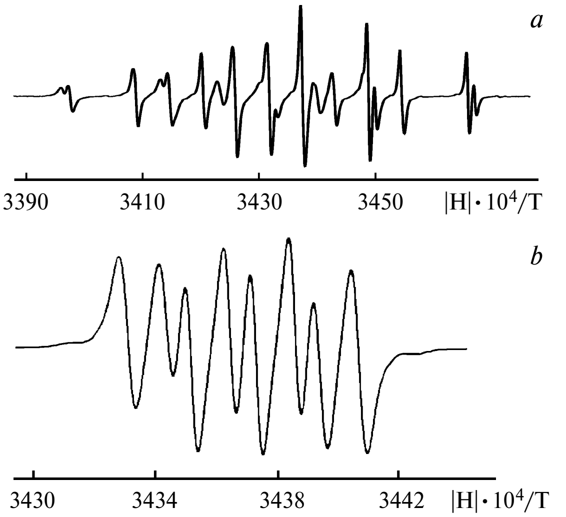


Fig. 2. The ESR spectra of complexes **13** (*a*) and **15** (*b*) in THF.

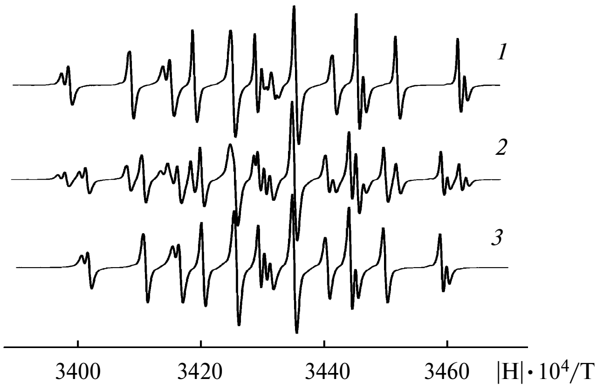


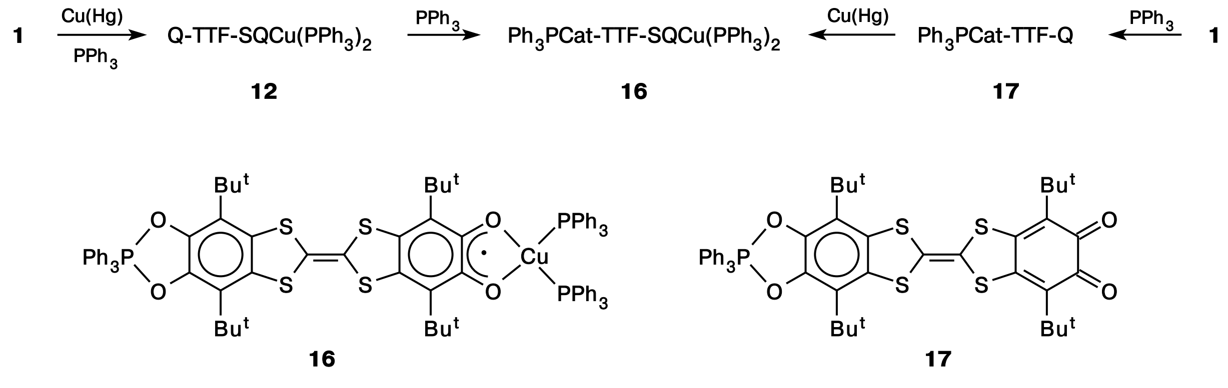
Fig. 3. Change in the ESR spectrum upon reduction of **1** with copper amalgam in the presence of PPh_3 in THF: *1* is the ESR spectrum of complex **12**; *2* is the superposition of the ESR spectra of complexes **12** and **16**; *3* is the ESR spectrum of complex **16**.

result in precipitation of green powders and no isotropic ESR signals are observed. The solids thus formed are likely the corresponding copper(I) complexes. This assumption is substantiated by the fact that the addition of equimolar amounts of di-*o*-quinone **1** to the compounds obtained results in their complete dissolution and the appearance of intense ESR spectra of complexes **12—15**.

Our attempt to obtain the binuclear copper(I) complex by direct reduction of di-*o*-quinone **1** with copper amalgam in the presence of PPh_3 in a sealed tube with ESR monitoring of the process led to observation of the new initial signal of complex **12** (Fig. 3) and a new ESR spectrum of a copper(I) complex with lower constants of splitting on the magnetic nuclei of copper and phosphorus. As the reaction proceeds, the intensity of the second spectrum increases stepwise while that of the first spectrum decreases. The second spectrum belongs to the catechol-semiquinone complex **16** formed upon oxidative addition of PPh_3 to the free quinone ring in the mono-*o*-semiquinone complex **12** (Scheme 2). It is known that *o*-quinones react with phosphines to form phospholane rings.[31] The reaction of **1** with copper amalgam in the presence of PPh_3 is accompanied by this side reaction (Scheme 2). In addition, complex **16** forms upon the reduction of phospholane **17** prepared by the reaction of **1** with PPh_3 with copper amalgam (see Scheme 2).[31] The ESR spectrum of compound **16** shows no splitting on the ^{31}P magnetic isotope containing in the phospholane ring.

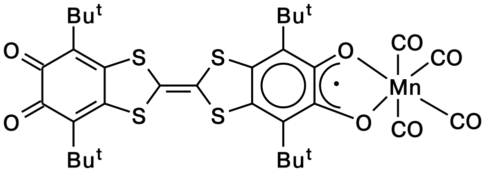
When a solution of **1** in THF mixed with $Mn_2(CO)_{10}$ was irradiated by the full spectrum of a HBO 50W/AC lamp equipped with a focusing device (UV region), the ESR spectrum appears as a sextet (Fig. 4, *a*) due to the HFC of the unpaired electron with the ^{55}Mn magnetic isotope (100%, $I = 5/2$, $\mu_N = 3.4687$);[26] this suggests the formation of the semiquinone complex **18** (Scheme 3). The addition of PPh_3 to the reaction mixture enables replacement of one CO group in the apical position of this complex to form the monophosphine derivative **19** (see Scheme 3) whose ESR spectrum displays an additional splitting on the magnetic ^{31}P nucleus (Fig. 4, *b*). At the same time, the constant of HFC with the manganese nucleus also increases (see Table 1).

Scheme 2

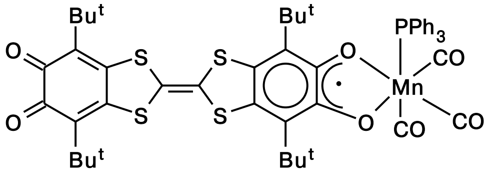


Scheme 3

$$\mathbf{1}\ \xrightarrow[-\mathrm{CO}]{1/2\,\mathrm{Mn_2(CO)_{10}}}\ \underset{\mathbf{18}}{\mathrm{Q\text{-}TTF\text{-}SQMn(CO)_4}}\ \xrightarrow[-\mathrm{CO}]{\mathrm{PPh_3}}\ \underset{\mathbf{19}}{\mathrm{Q\text{-}TTF\text{-}SQMn(CO)_3(PPh_3)}}$$



18



19

A number of paramagnetic heteronuclear complexes containing the three-reduced form of ligand **1** was successfuly prepared by analogy with triphenylantimony(v) 6-(*tert*-butyl)-4-[5-(*tert*-butyl)-2-methyl-3,4-dioxocyclohexa-1,5-dienyl]-3-methylcatecholate.[19] The oxidative addition of triphenylantimony to **1** at an equimolar reactant ratio led to *in situ* formation of a diamagnetic quinone-catecholate **20**, from which the bimetallic complexes **21**-**27** were generated following Scheme 4; the parameters of their isotropic ESR spectra are given in Table 1. The patterns of the ESR spectra of all semiquinone-catecholate derivatives is analogous to those of the monosemiquinone complexes with the same magnetic centers. No hyperfine coupling with the magnetic isotopes ^{121,123}Sb is observed. The distinctive features of the ESR spectra of all the catechol-semiquinone derivatives obtained including the trisodium complex **8** and complex **16** having the phospholane ring are the smaller of the splittings on the magnetic centers compared to the ESR spectrum of the monoreduced form of di-*o*-quinone **1** (see Table 1). It appears that this is due to a lower contribution of the metal orbitals to the molecular orbital of the complex that contains the unpaired electron in the case of semiquinone-catecholate.

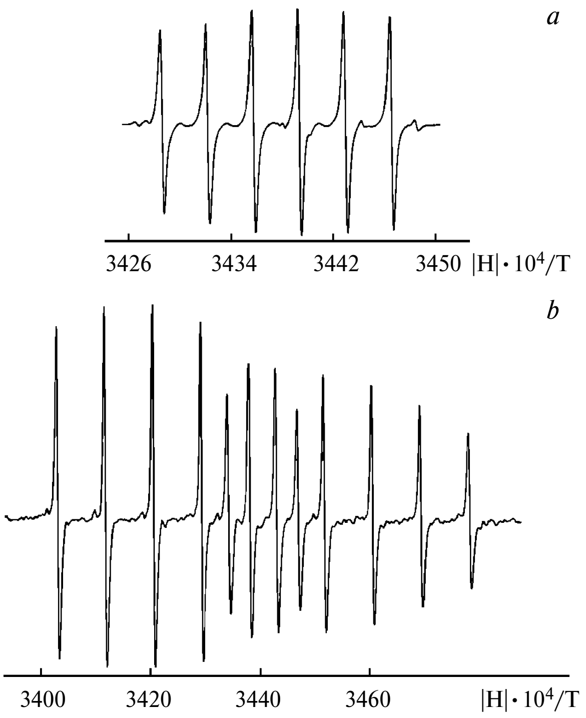


Fig. 4. The ESR spectra of complexes **18** (*a*) and **19** (*b*) in THF.

It should be noted that the paramagnetic derivative **27** formed in the reaction with hexaphenyldistannane was more stable than triphenyltin semiquinolate **11**; its ESR spectrum appeared as an intense singlet with satellites (Fig. 5) caused by the HFC of the unpaired electron with the magnetic isotopes of one tin atom remained unchanged for long. A high lability of the monosemiquinone complex **11** can be related to the addition of yet one triphenyltin fragment to the second quinone ring followed by elimination of the phenyl groups to form diamagnetic products.[35]

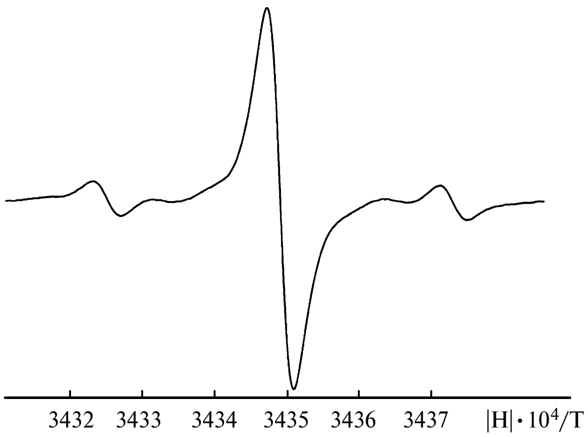
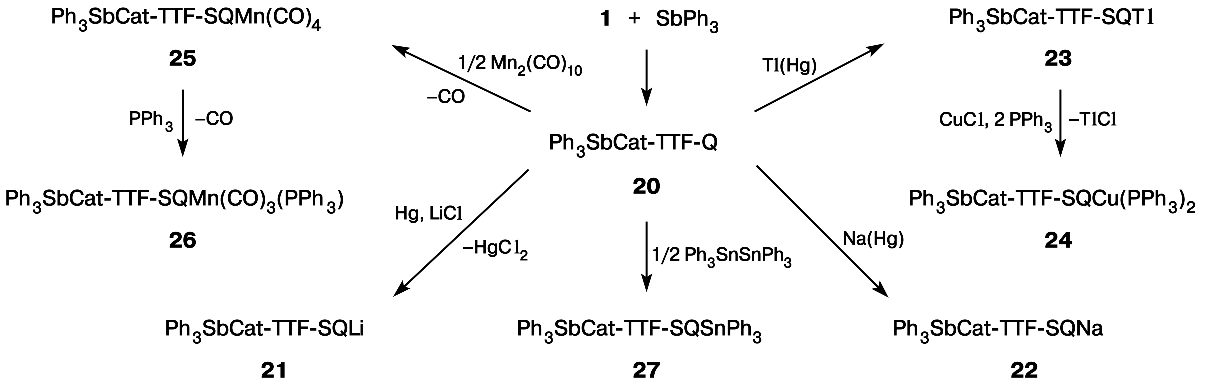
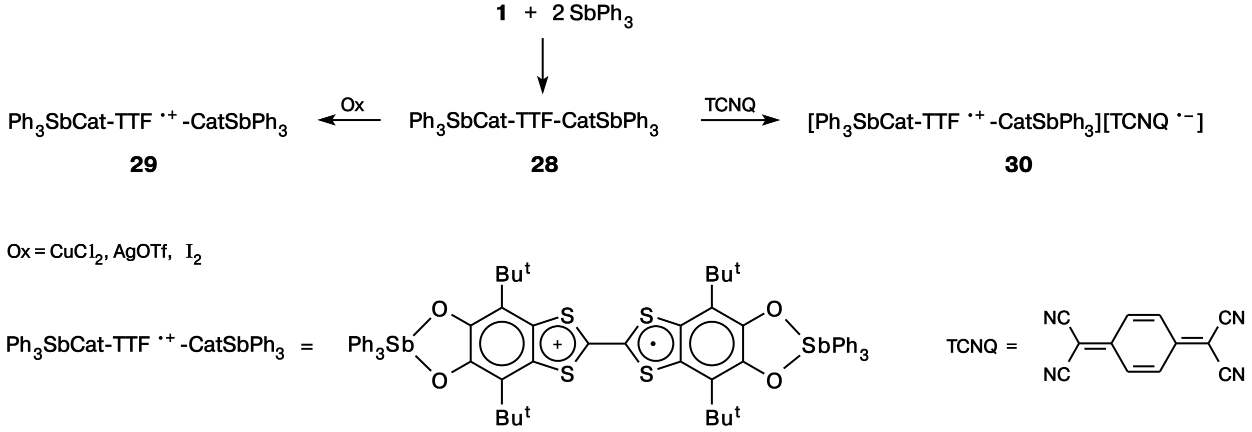


Fig. 5. The ESR spectrum of the binuclear complex **27** in THF.

Scheme 4



Scheme 5



All examples listed above charaterize the coordinating ability of di-*o*-quinone **1**, which enables realization of all possible reduced states to form the paramagnetic monosemiquinone (**2**—**5**, **9**—**15**, **18**, and **19**) and semiquinone-catecholate (**8**, **16**, and **21**—**27**) derivatives, two different doubly reduced forms (disemiquinone **7** and quinone-catecholate **20**), and the diamagnetic dicatecholate form of the completely reduced sodium dicatecholate (**6**).

All attempts to oxidize di-*o*-quinone **1** at the TTF fragment both in the electrochemical cell and using different chemical oxidizers (silver triflate, $CuCl_2$, I_2, Br_2, H_2O_2) resulted in the appearance of a singlet with $g = 2.0080$ in the ESR spectrum. By analogy with the oxidation of di-*p*-quinone having the TTF fragment,[36] this can be explained by the formation of the corresponding radical cation. However, the intensity of this signal is extremely low. In addition, the oxidized form was unstable and the signal disappeared irreversibly within a few hours.

The oxidation of the diamagnetic chelated triphenylantimony dicatecholate **28** generated *in situ* allows quantitative preparation of the radical cation derivatives. One-electron reduction of **28** with the silver and copper(II) salts, as well as with molecular iodine resulted in the radical cation **29** (Scheme 5) characterized by the singlet ESR signal with the *g*-factor (see Table 1) close to that of the radical cation formed upon the oxidation of **1**. The ab-

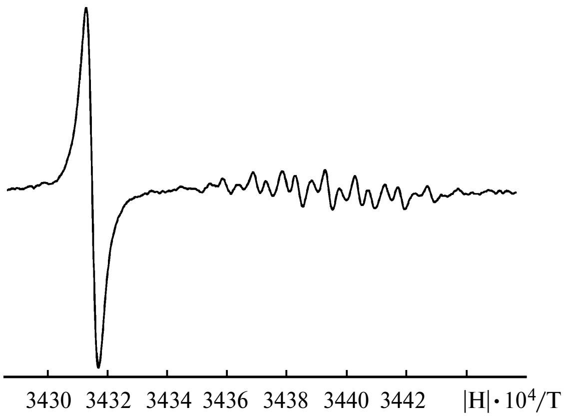


Fig. 6. The ESR spectrum of the radical salt **30** in THF.

sence of splitting on the magnetic isotopes ^{121,123}Sb confirms the fact that the unpaired electron in **29** is localized just on the TTF fragment and no semiquinone derivatives are produced in this case. The reaction of **28** with the strong organic π-electron acceptor TCNQ affords the radical salt **30** (see Scheme 5) whose ESR spectrum displays the corresponding singlet signal of the radical cation and a multiplet signal of the radical anion TCNQ$^-$ with the typical HFS (Fig. 6, see Table 1). The integrated intensities of these signals are in a 1 : 1 ratio, which confirms the formation of the stoichiometric compound **30**.

Experimental

ESR spectra were recorded on a Bruker EMX spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer in an evacuated cell made of molybdenum glass with an absorption layer thickness of 5 mm. IR spectra were recorded on a FSM-1201 FT-IR spectrometer.

Solvents were purified and dried according to conventional procedures.[37] Di-*o*-quinone **1** was synthesized according to the previously described procedure.[25] The samples of the paramagnetic derivatives **2—5**, **9—15**, **18**, and **19** for ESR studies were prepared in evacuated tubes in THF according to known procedures for the synthesis of semiquinone complexes.[11—13] All procedures for the synthesis and isolation of the sodium complexes **3** and **6—8** were performed *in vacuo* or in argon atmosphere.

The semiquinone-catecholate complex **16** was generated in THF solution by reduction of **1** with copper amalgam in the presence of excess PPh$_3$. The reaction was performed with continuous stirring in a sealed tube. The initially emerged ESR signal of the monosemiquinone complex **12** was transformed stepwise to the signal of complex **16** with the phospholane ring. The process completed within 5 days. The ESR signal of compound **16** was also recorded upon the addition of copper to a solution of phospholane **17** prepared according to a known procedure.[31]

Sodium monosemiquinolate (3). A solution of di-o-quinone **1** (0.1178 g, 0.2 mmol) in THF (40 mL) was agitated with sodium amalgam containing sodium (0.0046 g, 0.2 mmol) for a few minutes. The resultant dark-blue solution was filtered off and concentrated to 5 mL. After cooling to −20 °C, the dark-blue fine-crystalline complex **3** (0.0490 g, 40%) was isolated. The compound is insoluble in hydrocarbons, halogenated hydrocarbons, Et$_2$O, MeCN, and is partially soluble in MeOH. Found (%): C, 59.11; H, 5.87; Na, 3.82; S, 20.85. $C_{30}H_{36}NaO_4S_4$. Calculated (%): C, 58.89; H, 5.93; Na, 3.76; S, 20.96. IR, ν(C—O)/cm^{-1}: 1599, 1406, 1359. EAS (THF), λ_{max}/nm: 400 (ε 11000), 685 (ε 16000).

Sodium disemiquinolate (7) was obtained analogously. Sodium (0.0092, 0.4 mmol) was used for the reduction of **1** (0.1178 g, 0.2 mmol). Complex **7** (0.0381 g, 30%) was isolated as dark-green fine crystals from the green solution upon cooling. Compound **7** is insoluble in organic solvents, except for THF. Found (%): C, 56.55; H, 5.77; Na, 7.28; S, 20.11. $C_{30}H_{36}Na_2O_4S_4$. Calculated (%): C, 56.76; H, 5.72; Na, 7.24; S, 20.20. IR, ν(C—O)/cm^{-1}: 1403, 1352. EAS (THF), λ_{max}/nm: 390 (ε 25000), 990 (ε 13000).

The low yields of complexes **3** and **7** are explained by sufficiently high solubility in THF. Precipitation of the metal complexes using hexane affords the powder samples in 90% yield.

Sodium semiquinone-catecholate (8). A solution of **1** (0.1178 g, 0.2 mmol) in THF (30 mL) was agitated with sodium amalgam (0.0138 g, 0.6 mmol) until the solution color changed from violet to greenish-brown and a precipitate was formed. The resulted slurry was decanted, separated from mercury metal, and washed with THF to isolate the deep-brown fine-crystalline complex **8** (0.0921 g, 70%), which is insoluble in organic solvents. Found (%): C, 54.82; H, 5.51; Na, 10.37; S, 19.18. $C_{30}H_{36}Na_3O_4S_4$. Calculated (%): C, 54.77; H, 5.52; Na, 10.48; S, 19.50. IR, ν(C—O)/cm^{-1}: 1349, 1227, 1181.

Sodium dicatecholate (6) was prepared analogously to complex **8**. Sodium amalgam with an excess of metal (0.1840 g, 8 mmol) was used for the reduction of **1** (0.1178 g, 0.2 mmol). Upon agitation, a solution became virtually colorless and a golden yellow precipitate formed. Complex **6** was separated by decantation from an excess of amalgam to isolate a yellow fine-crystalline substance (0.1158 g, 85%) insoluble in organic solvents. Found (%): C, 53.13; H, 5.27; Na, 13.62; S, 18.50. $C_{30}H_{36}Na_4O_4S_4$. Calculated (%):C, 52.92; H, 5.33; Na, 13.51; S, 18.84. IR, ν(C—O)/cm^{-1}: 1229, 1184.

Complexes **3**, **7**, and **8** were obtained from compound **6** by the addition of di-*o*-quinone **1** (1.5, 1 or 0.5 equiv., respectively) to it.

Triphenylantimony monocatecholate **20** was synthesized *in situ* in THF by oxidative addition of triphenylantimony to di-*o*-quinone **1** (see Ref. 19) at a reactant ratio of 1 : 1. The resulted blue-green solution was used for the preparation of the semiquinone-catecholate complexes **21—27** according to the previously described procedures.[19]

Triphenylantimony dicatecholate **28** was prepared according to the analogous procedure[19] upon mixing of solutions of **1** and triphenylantimony in THF at a 1 : 2 molar ratio. The addition of slight amounts of the oxidizing reagents to the resulted diamagnetic solution led to the change in the solution color from green-yellow to deep-brown and the ESR spectrum displayed an intense singlet corresponding to the radical cation **29**. Anhydrous CuCl$_2$, silver triflate, and I$_2$ were used as the oxidizing agents.

The radical ion salt **30** was generated by addition of a solution of TCNQ in THF to a solution of triphenylantimonic dicatecholate **28** prepared *in situ* according to the procedure described above. The ESR spectrum of the resulted brown solution displayed the signal typical of the radical cations and radical anions contained in **30**.

The oxidation of **1** was performed using silver triflate, CuCl$_2$, I$_2$, Br$_2$ or a diluted solution of H$_2$O$_2$ in THF, CH$_2$Cl$_2$, and MeCN. In all cases, the solution color remained violet and the ESR signal (singlet, g = 2.0080) had low intensity and disappeared for a few hours.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 10-03-00788 and 10-03-00921) and the Council for Grants at the President of the Russian Federation (Program for Support of Leading Scientific Schools of the RF, Grant NSh-7065.2010.3). This research work was performed as a part of the Federal Target Progam "Academic and Teaching Staff of Innovative Russia" in 2009—2013 (GK P839 of May 25, 2010).

References

1. *Molecular Electronics*, Ed. G. J. Ashwell, Wiley, Chichester, 1992.
2. *Molecular Electronics and Molecular Electronics Devices*, Ed. K. Sienik, CRC Press, Boca Raton, FL, 1994.
3. *Introduction to Molecular Electronics*, Eds M. C. Petty, M. R. Bryce, D. Bloor, Oxford University Press, New York, 1995.
4. V. I. Ovcharenko, R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1999, **68**, 345].
5. A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.*, 2004, **104**, 5243.
6. T. Enoki, A. Miyasaki, *Chem. Rev.*, 2004, **104**, 5449.
7. E. Coronado, P. Day, *Chem. Rev.*, 2004, **104**, 5419.
8. O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
9. K. Itoh, M. Kinoshita, *Molecular Magnetism*, *New Magnetic Materials*, Gordon, Breach, Amsterdam, 2000.
10. O. Sato, J. Tao, Y.-Zh. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152.
11. G. A. Abakumov, V. K. Cherkasov, *Metallorg. Khim.*, 1990, **3**, 838 [*Organomet. Chem. USSR* (*Engl. Transl.*), 1990, **3**, 426].
12. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219—221**, 415.
13. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216—217**, 99.
14. A. I. Poddel´sky, V. K. Cherkasov, G. A. Abakumov, *Coord. Chem. Rev.*, 2009, **253**, 291.
15. G. A. Abakumov, V. I. Nevodchikov, V. A. Kuropatov, B. C. Noll, C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 6117.
16. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, V. A. Kuropatov, G. T. Yee, C. G. Pierpont, *Inorg. Chem.*, 2001, **40**, 2434.
17. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, N. O. Druzhkov, V. A. Kuropatov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 904 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 875].
18. A. V. Piskunov, V. K. Cherkasov, N. O. Druzhkov, G. A. Abakumov, V. N. Ikorskii, *Izv. Akad. Nauk, Ser. Khim.*, 2005, **54**, 1580 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1627].
19. V. K. Cherkasov, E. V. Grunova, G. A. Abakumov, *Izv. Akad. Nauk, Ser. Khim.*, 2005, **54**, 2004 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2067].
20. A. I. Poddel´sky, A. V. Piskunov, N. O. Druzhkov, G. K. Fukin, V. K. Cherkasov, G. A. Abakumov, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2563.
21. F. Wudl, G. M. Smith, E. J. Hufnagel, *J. Chem. Soc.*, *Chem. Commun.*, 1970, 1453.
22. J. Ferraris, D. O. Cowan, V. V. Walatka, Jr., J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.
23. *Organic Conductors. Fundamentals and Applications*, Ed. J. P. Farges, Marcel Dekker, New York, 1994.
24. T. Ishiguro, K. Yamaji, G. Saito, *Organic Superconductors*, Springer-Verlag, Berlin—Heidelberg, 1998.
25. V. A. Kuropatov, S. V. Klementieva, G. K. Fukin, S. Yu. Ketkov, A. S. Mitin, Yu. G. Budnikova, V. K. Cherkasov, G. A. Abakumov, *Tetrahedron*, 2010, **66**, 7605.
26. B. A. Goodman, J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 136.
27. G. A. Abakumov, V. A. Muraev, G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1974, **215**, 1113 [*Dokl. Chem.* (*Engl. Transl.*), 1974].
28. V. A. Muraev, G. A. Abakumov, G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1974, **215**, 159 [*Dokl. Chem.* (*Engl. Transl.*), 1974].
29. G. A. Abakumov, N. Yu. Kabarova, V. K. Cherkasov, *Metallorg. Khim.*, 1992, **5**, 1145 [*Organomet. Chem. USSR* (*Engl. Transl.*), 1992, **5**].
30. G. A. Abakumov, A. V. Lobanov, V. K. Cherkasov, G. A. Razuvaev, *Inorg. Chem. Acta*, 1981, **49**, 135.
31. V. A. Muraev, V. K. Cherkasov, G. A. Abakumov, G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1977, **236**, 620 [*Dokl. Chem.* (*Engl. Transl.*), 1977].
32. A. V. Krashilina,, Ph. D. Thesis (Chem.), Inst. of Metallorg. Chem. of the RAS, Nizhnii Novgorod, 2004, 118 pp.
33. G. A. Abakumov, V. K. Cherkasov, A. V. Krashilina, I. L. Eremenko, S. E. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, **47**, 2333 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 2262].
34. G. A. Abakumov, A. V. Krashilina, V. K. Cherkasov, L. N. Zakharov, *Dokl. Akad. Nauk*, 2003, **391**, 343 [*Dokl. Chem.* (*Engl. Transl.*), 2003, **391**, 185].
35. H. B. Stegmann, R. Schrade, H. Saur, P. Schuler, K. Scheffler, *J. Organomet. Chem.*, 1981, **214**, 197.
36. F. Dumur, N. Gautier, N. Gallego-Planas, Y. Sahin, E. Levillain, N. Mercier, P. Hudhomme, M. Masino, A. Girlando, V. Lloveras, J. Vidal-Gancedo, J. Veciana, C. Rovira, *J. Org. Chem.*, 2004, **69**, 2164.
37. A. Weissberger, E. S. Proskauer, J. A. Riddick, E. E. Toops, *Organic Solvents, Physical Properties and Methods of Purification*, Interscience Publ., New York—London, 1955.

Received July 21, 2010