ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 4, pp. 790–799. © Pleiades Publishing, Ltd., 2010.
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Complexes of the 14th Group Elements with Tridentate Redox-Active Ligand

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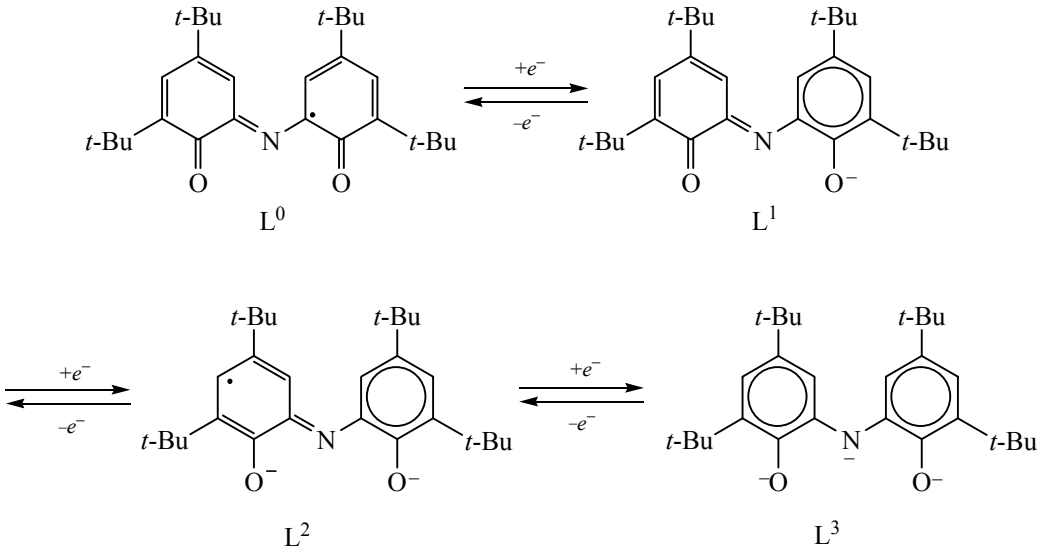
Received July 23, 2009

Abstract—New methods of synthesis of the 14th group metal (Si, Sn, Pb) complexes containing a redox-active ligand, 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine, in various redox states were developed. New compounds were studied by the ESR spectroscopy in solutions. The redox properties of the paramagnetic tin compounds are characterized by the cyclic voltammetry. The solvent and temperature effect on the ESR spectra parameters of paramagnetic complexes of Sn(IV)and Pb(IV) was revealed.

DOI: 10.1134/S1070363210040195

Chemistry of metal complexes with redox-active ligands, *o*-quinones and their N-heteroanalogs, was actively developed in recent years [1]. An important property of such complexes of nontransition elements is their ability to enter in the redox transformations at the expense of the ligand, which reduces or oxidizes the organic substrate coordinated to the metal rather than the complex-forming atom itself [2, 3]. This property substantially expands the redox possibilities of the nontransition metal complexes, for which a large number of redox states is not typical. One of promising ligands for preparation of such metal complexes is 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine. Being bound in the complex with metal, this ligand can exist in four different redox states (Scheme 1).

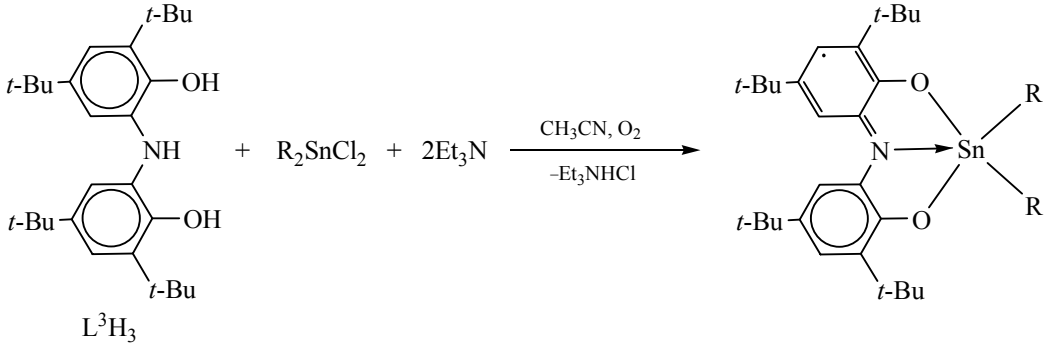
Scheme 1.



The neutral (L^0) and the doubly reduced (L^2) forms are radicals, whereas the mono- (L^1) and trianion (L^3) are diamagnetic. The results of numerous studies are indicative of the tridentate coordination of all forms L^0–L^3 to the metal [4–13]. Up till now, the main method for preparation of metal complexes of this tridentate ligand was the template synthesis, including the reaction of 3,5-di-*tert*-butylpyrocatechol with the salts of the corresponding metals in alcohol solution in the presence of ammonia and the air oxygen [4, 7–10]. However, this method has some shortcomings: first, this is the presence of admixtures of the side products, and, second, the impossibility to obtain compounds with predetermined oxidation states of the ligand. Rather recently, for preparation of metal complexes with 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine the protonated salt of the ligand L^3H_3 [12] and its trifluoroacetic salt [13] were used as the reagents. In this work we report on the studies on the preparation of the 14th group element (Si, Sn, Pb) complexes based on the radical form of the ligand L^2 and their investigation by the ESR spectroscopy.

First the derivatives of the type L^2MAr_2 (M = Ge, Sn, Pb) were prepared by the template synthesis by Stegmann et al. [14–16]. Later, compounds $(L^2)_2Sn$, $(L^2)_2Ge$ [9, 10], $(L^1)_2Pb$ [10], L^2SnMe_2, and $L^1Sn(Cl)_2Bu$ [8] were prepared by the same procedure. In the present study we found that the tin compounds L^2SnR_2 (R = Me, Et, *n*-Bu, *t*-Bu, Ph) could be prepared in a high yield by the reaction of bis(2-hydroxy-3,5-di-*tert*-butylphenyl)amine (L^3H_3) with diorganyl halides in the presence of triethylamine and air oxygen. The reaction in acetonitrile is completed in several minutes and is followed by the appearance of intense violet color of the reaction mixture. The formed paramagnetic tin complexes **I–V** are isolated from the reaction mixture as fine violet crystals (Scheme 2).

Scheme 2.



R = Me (**I**), Et (**II**), *n*-Bu (**III**), *t*-Bu (**IV**), Ph (**V**).

The obtained compounds are resistant to the action of the air oxygen and moisture both in the crystalline state and in solution. Complexes **I–V** are readily soluble in many nonpolar organic solvents. The solutions of the obtained tin complexes possess well resolved ESR spectra (Fig. 1a). Their hyperfine structure (HFS) is due to hyperfine interaction (HFI) of the unpaired electron with magnetic nuclei of the two pairs of equivalent protons ^1H (99.98%, I = 1/2, μ_N = 2.7928), magnetic nucleus ^{14}N (99.63%, I = 1, μ_N = 0.4037) and the satellite splitting on the magnetic tin isotopes ^{117}Sn (7.68%, I = 1/2, μ_N = 1.000), ^{119}Sn (8.58%, I = 1/2, μ_N = 1.046) [17].

Parameters of the ESR spectra of compounds **I–V** are given in Table 1. Precise values of the HFI values were obtained by simulation of the spectra using the Win EPR Simfonia program. The fact that we observe HFI with two pairs of equivalent protons is indicative of delocalization of the electron density to two aromatic rings of the organic ligand. This is also supported by the presence of an intense absorption band in the near-IR spectrum at 1000 nm. The parameters of the ESR spectrum for complex **V** are close to those described earlier [14].

The ability of the obtained tin paramagnetic complexes to participate in the redox transformations was studied by the method of cyclic voltammetry by the example of compounds **I**, **II**, and **V**. For complexes **I, II, V** in dichloromethane three redox steps were observed on a glass carbon electrode (Table 2). The

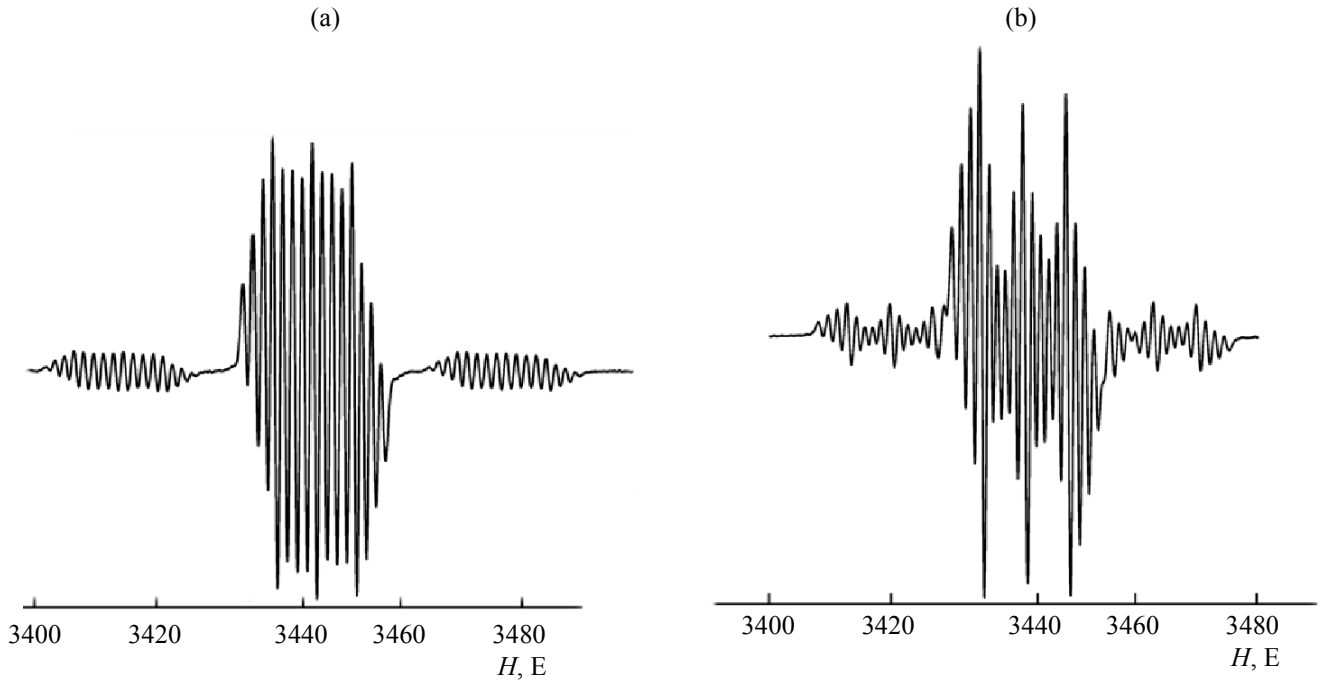
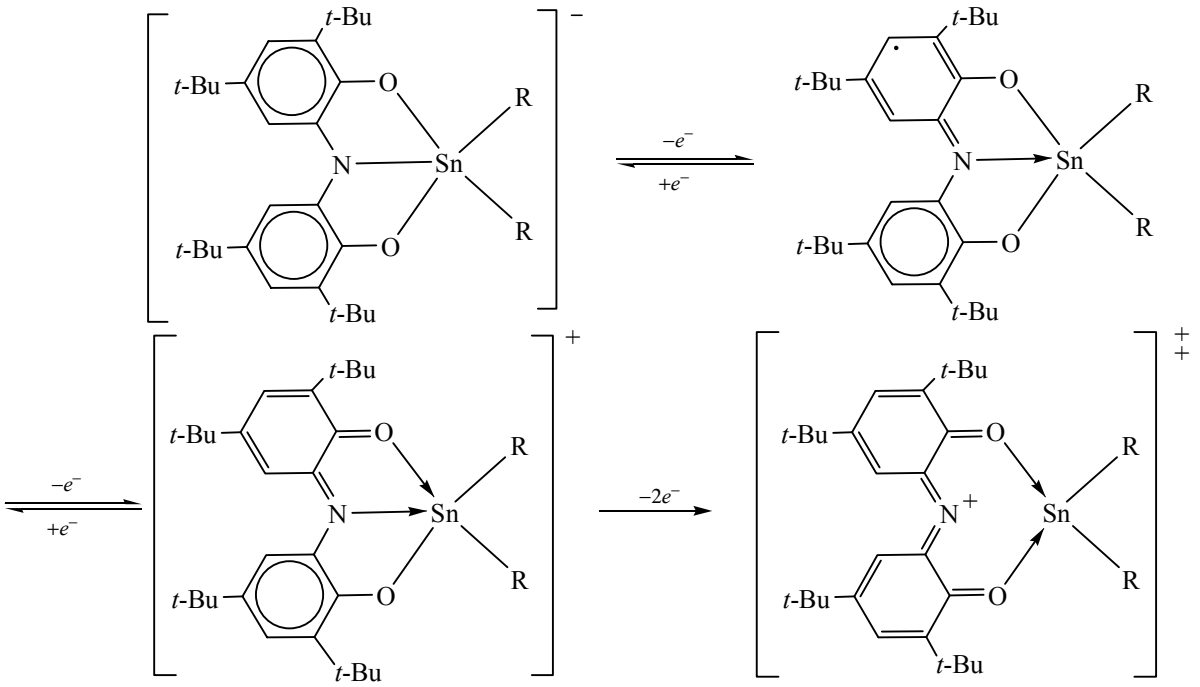


Fig. 1. Isotropic ESR spectra in hexane: (a) complex **IV** and (b) complex **VIII**. T = 290 K.

studied tin complexes display two reversible one-electron processes (Fig. 2, Scheme 3).

The observed redox transformations correspond to variation of the oxidation degree of the ligand between the tri-, di, and mono-anionic forms. Judged from the values of the reversibility coefficients (Table 2), the formed reduced/oxidized forms of complexes are relatively stable during the time of the experiment. While for the transition metal complexes an additional

Scheme 3.



R = Me (**I**), Et (**II**), Ph (**V**).

Table 1. Parameters of ESR spectra for solutions of paramagnetic compounds in hexane. $T = 290$ K

Comp. no.	a_i(2H), E	a_i(2H), E	a_i(^{14}N), E	a_i(M),[a] E	g_i
I	1.54	3.09	6.59	50.72	2.0035
II	1.75	2.98	6.49	55.90	2.0035
III	1.64	3.11	6.54	55.30	2.0026
IV	1.64	3.12	6.40	64.60	2.0031
V	1.50	3.27	6.67	45.80	2.0028
VII	1.68	3.23	7.06	35.70	2.0020
VIII	1.55	3.03	7.06	42.99	2.0023
IX	1.28	3.00	5.63	7.06	2.0031
L^0	2.80	4.10	7.50	–	2.0036
X	1.70	3.60	7.60	8.30	2.0033

[a] For **I–V**: M = ^{117,119}Sn; **VII, VIII**: M = ^{207}Pb; **IX**: M = ^{29}Si; **XI**: M = H.

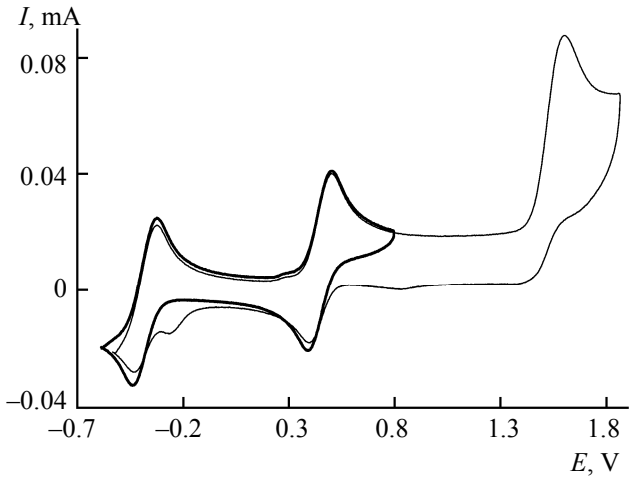


Fig. 2. Cyclic voltammogram of complex **I** (CH_2Cl_2, V = 0.2 V s^{-1}, Ag/AgCl/KCl, $C = 3\times10^{-3}$ mol l^{-1}, glass carbon electrode, Ar, 0.1 M Bu_4NClO_4).

reversible transition corresponding to the formation of the neutral paramagnetic form L^0 was detected by electrochemical methods [6, 18], for the tin compounds a two-electron anode stage (E = 1.57 V) characterizing the formation of an unstable cationic form of the ligand is observed [19]. The oxidation is followed by the subsequent chemical process of decoordination of the ligand and decomposition of the complex (Fig. 2). With this, in the reverse branch of the cyclic voltammogram the peak of reduction of the products of decomposition is observed at –0.3 V. For reversible one-electron redox transitions the value of $E_{1/2}$ is a thermodynamic value which allows the estimation of the energy of the molecular orbital most strongly changed during the redox reaction. The obtained values of the difference ΔE between the $E_{1/2}^{Ox.1}$ and $E_{1/2}^{Red.1}$ allow the estimation of the HOMO–LUMO energy gap. The calculated values are equal to 0.83 and 0.86 V for complexes **I, II**, and **V**, respectively. On going from the monocationic form of the complex to its monoanionic form the value of ΔE also characterizes the stability of the formed neutral paramagnetic complex. The obtained constants of conproportionation exceed 1×10^6 indicating a wide delocalization of the charge and the spin in the neutral complex, as proved by the ESR studies. The effect of substituents at the tin atom is manifested in the values of potentials shifted by 0.1 V for complex **V** containing acceptor phenyl groups as compared with the alkyl derivatives **I** and **II**.

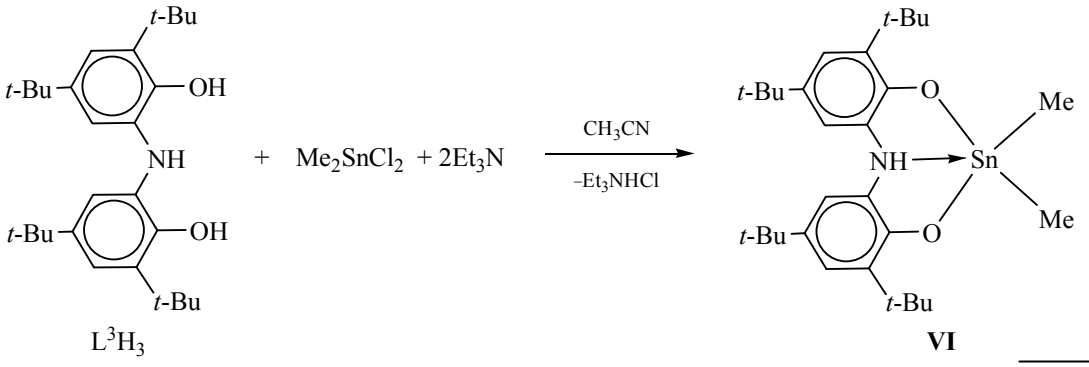
The synthesis of compounds **I–V** by Scheme 2 proceeds via the step of formation of the diamagnetic tin complex, which upon further oxidation with the air oxygen affords paramagnetic products. Thus, L^3H_3 reacts with dimethyldichlorostannane in the absence of air oxygen in the presence of triethylamine to give the aminodiphenolate tin complex according to Scheme 4. The formed complex **VI** was isolated from the reaction mixture as a fine crystalline white compound. The composition and the structure of this complex is proved by the data of the IR and ^{1}H NMR spectro-

Table 2. Electrochemical characteristics of complexes **I**, **II**, and **V** [Glass carbon electrode, CH_2Cl_2, V = 0.2 V s^{-1}, 0.1 M NBu_4ClO_4, $C = 3\times10^{-3}$ mol l^{-1}, Ar, ref. Ag/AgCl/KCl(sat.)]

Comp. no.	$E_{1/2}^{Ox/Red}$, V[a]	I_c/I_a[b]	n[c]	$E_{1/2}^{Ox.1}$, V[d]	I_c/I_a	n	$E_p^{Ox.2}$, V	ΔE, V[e]
I	–0.40	0.85	1	0.43	0.91	1	1.60	0.83
II	–0.44	0.85	1	0.39	0.95	1	1.58	0.83
V	–0.30	0.90	1	0.56	0.92	1	1.70	0.86

[a] $E_{1/2}^{Ox/Red}$ is the redox half-wave potential. [b] I_c/I_a is the coefficient of reversibility. [c] n is the number of transferred electrons relative to the standard (ferrocene). [d] $E_p^{Ox.2}$ is the oxidation peak potential. [e] $\Delta E = E_{1/2}^{Ox.1} - E_{1/2}^{Red.1}$.

Scheme 4.

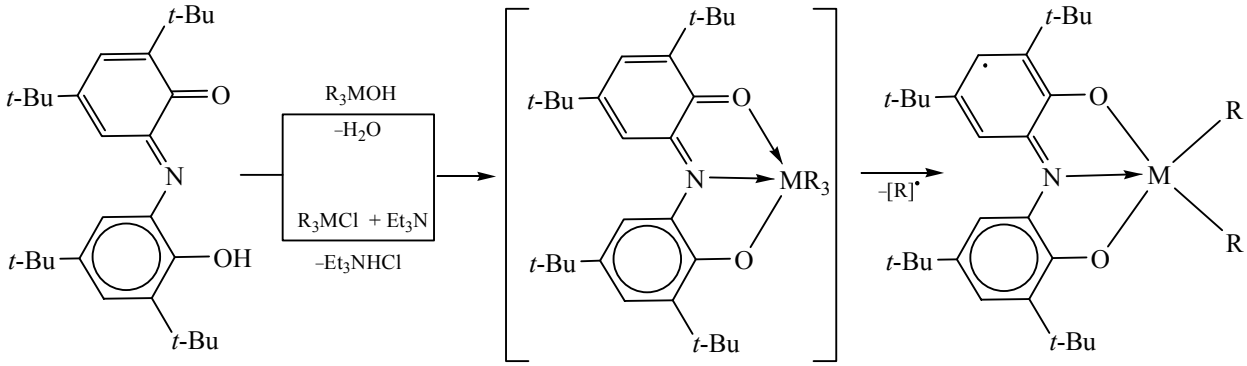


L^3H_3 **VI**

scopy and the elemental analysis. Upon contact of the solution of complex **VI** with air oxygen it immediately turns violet and in the ESR spectrum the signal appears which is indicative of formation of compound **I**.

It should be noted that the preparation of paramagnetic tin(IV) complexes **I–V** is possible when using 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (L^1H) as a reagent. Thus, reaction of Ph_3SnOH with L^1H in methanol leads to the formation of the paramagnetic product **V** (Scheme 5). In the first stage of the reaction the reaction mixture is green, that corresponds to the formation of the metal complex containing the deprotonated form of ligand L^1 [5]. Then apparently occurs the elimination of the hydrocarbon radical and the formation of the metal complex containing the ligand in the dianion-radical form (Scheme 5), which is followed by appearance of violet color and the corresponding signal in the ESR spectrum. Introduction of triethylamine into the reaction mixture allows performing the reaction not only with metal hydroxides but also with the corresponding triorganyl halides. This procedure was used to generate paramagnetic lead(IV) compounds in solution. The obtained paramagnetic lead complexes demonstrate well resolved ESR spectra, characterized by the HFI of the unpaired electron with magnetic nuclei of the two pairs of equivalent protons, magnetic isotope ^{14}N, and the satellite splitting on the magnetic lead isotope ^{207}Pb (22.1%, $I = 1/2$, $\mu_N = 0.5926$) [17]. The parameters of the ESR spectrum of the phenyl complex **VII** coincide with those reported earlier in [15], and for compound **VIII** the spectrum is obtained for the first time (Fig. 1b). Parameters of the ESR spectra for compounds **VII** and **VIII** are given in Table 1.

Scheme 5.



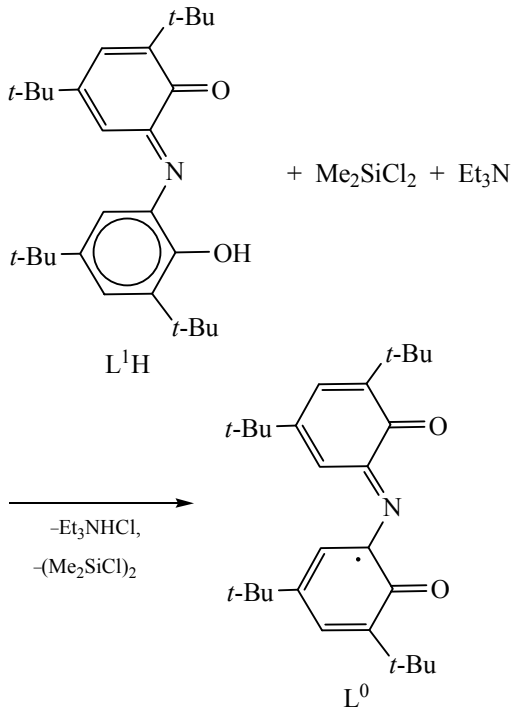
L^1H **V, VII–IX**

M = Sn, R = Ph (**V**), M = Pb, R = Ph (**VII**), Et (**VIII**); M = Si, R = Me (**IX**).

High stability to decomposition of the tin and lead paramagnetic complexes on the basis of the tridentate O,N,O-redox-active ligand suggested a possibility of its use for generation of paramagnetic complexes containing the alkylsilyl group, whose preparation on the basis of *o*-quinones seemed impossible [20]. The dimethylsilyl complex **IX** was synthesized by Scheme 5. The paramagnetic silicon complex **IX** in solution gives well resolved ESR spectrum. It represents a triplet (1:1:1) of triplet (1:2:1) of triplets (1:2:1). In the spectrum the HFI is observed of the unpaired electron with magnetic nuclei of the two pairs of equivalent protons and nitrogen atom and, besides, the satellite splitting on the magnetic silicon isotope ^{29}Si (4.67%, I = 1/2, μ_N =-0.5553) [17] (Fig. 3a). Parameters of the ESR spectrum of compound **IX** are given in Table 1.

Unexpectedly, the use of dimethyldichlorosilane in the similar reaction led to other products. The ESR spectrum observed during the reaction (Fig. 3b) is also a triplet (1:1:1) of triplet (1:2:1) of triplets (1:2:1). However, the values of the HFI constants with protons and the nitrogen magnetic isotope ^{14}N substantially differ from those observed for complexes **I–V, VI–IX**, besides the satellite splitting on the silicon magnetic isotope is absent. Based on these data, the spectrum was assigned to the neutral form of the ligand L^0 (Scheme 6).

Scheme 6.



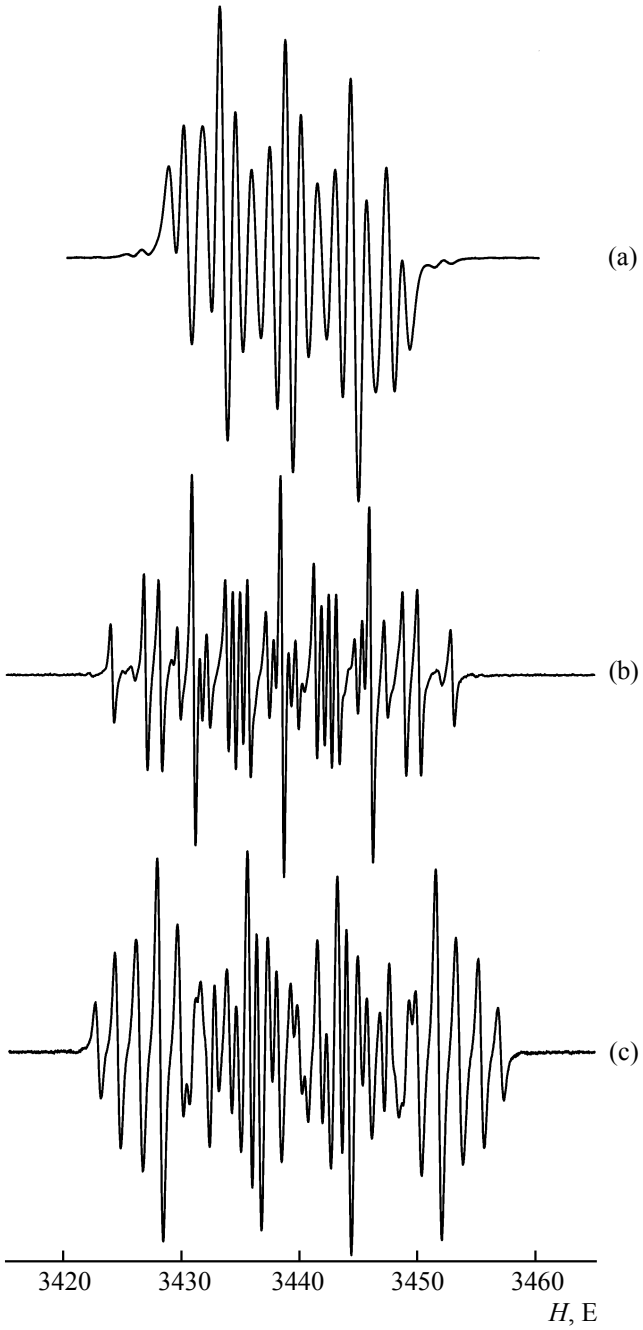
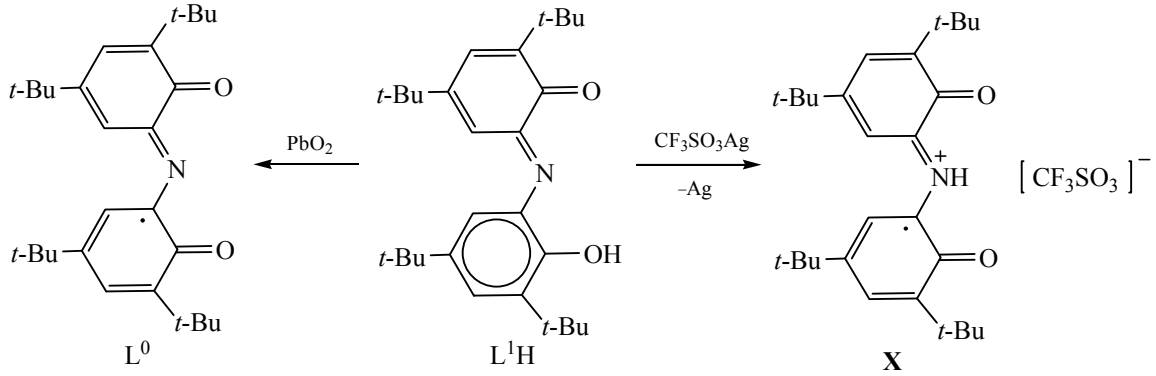


Fig. 3. Isotropic ESR spectra in hexane: (a) complex **IX,** (b) radical L^0, and (c) radical **X**. T = 290 K.

To confirm this assumption, we attempted an independent synthesis of radical L^0. Thus, during oxidation of L^1H with lead dioxide in hexane (Scheme 7) the ESR spectrum is observed corresponding to the radical form of the ligand L^0 and identical to that registered in the reaction of Scheme 6. At the same time, the oxidation of L^1H with silver triflate (Scheme 7) gives

the ESR spectrum corresponding to the radical-cation salt of the ligand **X** (Fig. 3c). HFI in this spectrum, along with the two pairs of protons and the nitrogen atom, causes an additional splitting on the hydrogen atom connected to nitrogen with the HFI constant a_i(H) = 8.3 Oersted.

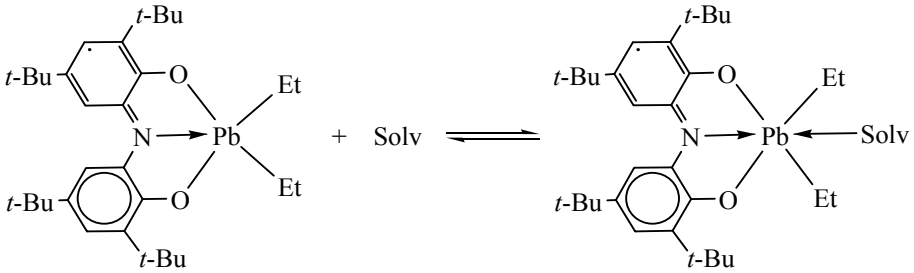
Scheme 7.



It should be mentioned that earlier attempts to registrate the ESR spectrum belonging to radical L^0 failed. Ivakhnenko et al who studied the condensation of 3,5-di-*tert*-butyl-*o*-benzoquinone with 4,6-di-*tert*-butyl-*o*-aminophenol suggested its formation in the course of the studied reaction but in the ESR spectrum they observed only the signal corresponding to the phenoxazine structure, the product of the intramolecular cyclization of radical L^0 [21].

In the present work we have established that parameters of the ESR spectra of paramagnetic complexes of tin **I–V** and lead **VII, VIII** substantially depend on the nature of the solvent. Earlier, the dependence of this type was observed for the o-semiquinone [22, 23] and o-iminosemiquinone [24] thallium complexes. Let us consider this phenomenon in more detail by the example of the lead diethyl complex **VIII**. As the donor number of the solvent [25] increases the HFI constant $a_i(^{207}\text{Pb})$ decreases (Fig. 4).However the HFI constants with the hydrogen and nitrogen nuclei remain unchanged within the error of measurement. Therefore, the variations of $a_i(^{207}\text{Pb})$ are connected with variation of the geometry of the coordination sphere of the metal. In the solvated form the HFI constant with the metal should be smaller. This is due to the alteration of the hybridization of the metal atom from sp^3d to sp^3d^2. Therefore the fraction of the *s*-character, which makes the largest contribution to the HFI of the unpaired electron with the metal, decreases. The equilibrium of the solvation of the lead complex can be illustrated by Scheme 8.

Scheme 8.



The character of the ESR spectrum is determined by the difference in the constants of the nonsolvated and solvated forms $a_{io}(^{207}\text{Pb})$–$a_{is}(^{207}\text{Pb})$ and the frequency of formation and decomposition of the solvate p [26]. For p >> $a_{io}(^{207}\text{Pb})$–$a_{is}(^{207}\text{Pb})$ (fast exchange) one signal with the averaged constant is observed. However, if p << $a_{io}(^{207}\text{Pb})$–$a_{is}(^{207}\text{Pb})$ (slow exchange), the spectrum is a superposition of the spectra of the nonsolvated and solvated forms of the complex. In our case, one signal is observed in all

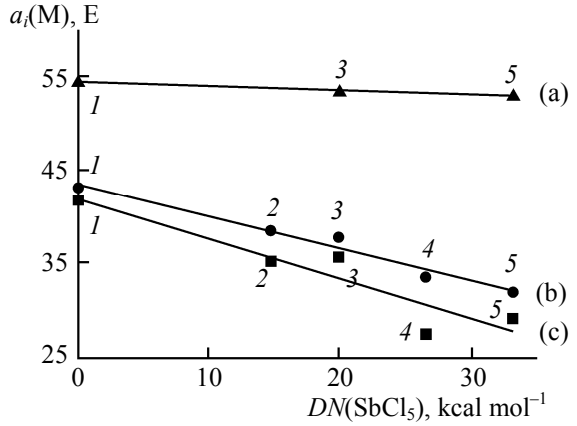


Fig. 4. Dependence of the HFI constants $a_i(^{117,119}Sn)$ for complex (a) **II** and $a_i(^{207}Pb)$ for (b) complexes **VIII,** and (c) **VII** on the donor number of the solvent. T = 290 K. (*1*) toluene, (*2*) dioxane, (*3*) THF, (*4*) DMF, and (*5*) pyridine.

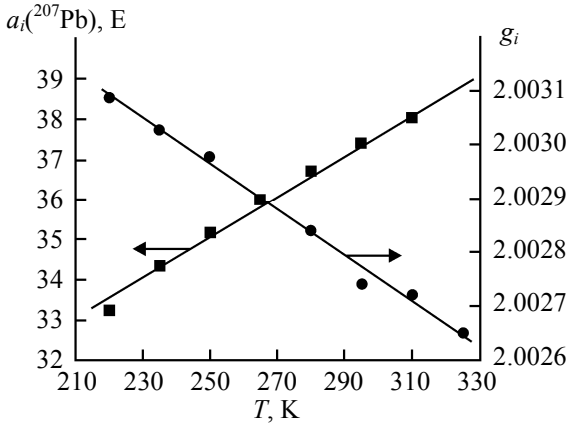


Fig. 5. Temperature dependence of HFI constant $a_i(^{207}Pb)$ and g_i-factor of complex **VIII** in THF.

solvents, which is indicative of a large value of p, and, hence, of a low stability of the solvate formed.

The equilibrium position (Scheme 8) depends on the temperature, so that it is shifted to the right with the decrease in the temperature. It is confirmed by the dependence of both the value of $a_i(^{207}Pb)$ and the g_i-factor on the temperature. When the temperature rises the concentration of the solvated form of the complex decreases; in the ESR spectrum this results in an increase of the HFI constant with the lead magnetic isotope and a decrease of the g_i factor (Fig. 5).

The replacement of the ethyl groups at the lead atom by phenyls on going from complex **VIII** to compound **VII** does not change the above trends. However, the dependence $a_i(^{207}Pb)$–$f(DN)$ (Fig. 4) has much larger scattering of the experimental points from the linear approximation. This indicates the presence of other factors affecting the equilibrium. One of them can be steric hindrances to coordination of the donor molecule of the solvent to the sterically overcrowded lead coordination center containing more bulky aryl substituents.

A good correlation between the HFI constant with magnetic isotopes of the metal and the donating power of the solvent is also observed for the tin paramagnetic complex **II**. However, variations of the $a_i(^{117,119}Sn)$ value are less significant. This suggests that the equilibrium of solvation for the tin complex is much more biased to the left than in the case of the analogous lead derivatives. The latter is explained by the smaller covalent radius of tin as compared with lead [17].

EXPERIMENTAL

The solvents were purified by standard procedures [27]. Commercial triethylamine, Me_2SiCl_2, Me_3SiCl (all Aldrich) were used. Organic derivatives of tin and lead were synthesized by the known procedures [28]. Bis(2-hydroxy-3,5-di-*tert*-butylphenyl)amine (L^3H_3) and 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (L^1H) were prepared as described in [29].

IR spectra were recorded on a FTIR spectrometer FCM 1201 in mineral oil in the 4000–400 cm^{-1} range. ESR spectra were taken of a Bruker EMX spectrometer. Diphenylpicrylhydrazyl was used as a standard to determine the g-factor (g = 2.0037). ^{1}H NMR spectra for solutions in $CDCl_3$ were registered on a Bruker DPX-200 spectrometer (200 MHz) with Me_4Si as an internal reference. Electron absorption spectra were obtained on a Perkin-Elmer Lambda 25 spectrometer.

Oxidation potentials were measured by the cyclic voltammetry (CVA) in a three-electrode cell in the argon atmosphere using a IPC-pro potentiostat, working electrode was a stationary glass-carbon electrode of 2 mm diameter, auxiliary electrode was a platinum plate (S = 18 mm^2), reference electrode was an Ag/AgCl/KCl with waterproof diaphragm. The potential sweep rate was 0.2 V s^{-1}. Background electrolyte was 0.1 M Bu_4NClO_4 (99%, Acros) twice crystallized from aqueous EtOH and dried in a vacuum for 48 h at 50°C. Dichloromethane was

purified and dried by the known procedures [27, 30]. The concentration of the studied complexes was 0.003 mol l^{-1}.

Synthesis of complexes I–V. To a solution of diorganyltin(IV) halide (Me_2SnCl_2 0.21 g, 0.94 mmol; Et_2SnCl_2 0.23 g, 0.94 mmol; Bu_2SnCl_2 0.29 g, 0.94 mmol; *t*-Bu_2SnCl_2 0.29 g, 0.94 mmol; Ph_2SnCl_2 0.32 g, 0.94 mmol) and bis(2-hydroxy-3,5-di-*tert*-butylphenyl)amine (0.4 g, 0.94 mmol) in 20 ml of acetonitrile in the air 0.26 ml of triethylamine was added resulting in the appearance of intense violet color and the formation of fine crystalline violet precipitate. The precipitate obtained was filtered off on a glass frit.

Complex I. Yield 0.40 g, 0.70 mmol, 74 %. Found, %: C 63.17; H 8.23; N 2.33; Sn 20.55. Calculated, %: C 63.06; H 8.11; N 2.45; Sn 20.78. $C_{30}H_{46}NO_2Sn$. IR spectrum, ν, cm^{-1}: 9877.4 s, 1520.8 w, 1478 s, 1446 s, 1418.3 m, 1359.6 s, 1250 w, 1231.3 s, 1178.5 s, 1110.8 s, 1044.2 s, 1023.3 m, 1008.3 m, 954.6 w, 932.7 w, 907.8 m, 847.1 m, 771.5 m, 727.7 m, 715.8 m, 663 w, 640 w, 603 w, 562 w, 533 w, 507 w, 465 w, 559 w, 437 w. UV spectrum, hexane, λ (ε, l cm^{-1} mol^{-1}): 285 (4800), 371 (11700), 392 (12900), 546 (2000), 1006 (8400).

Complex II. Yield 0.38 g, 0.63 mmol, 67%. Found, %: C 64.24; H 8.53; N, 2.31; Sn 19.72. Calculated, %: C 64.12; H 8.41; N, 2.34; Sn 19.8. $C_{32}H_{50}NO_2Sn$. IR spectrum, ν, cm^{-1}: 9877.4 s, 1477 s, 1418.3 s, 1360.1 s, 1324.5 s, 1318.6 s, 1275.2 w, 1232.7 s, 1191.2 s, 1177.4 s, 1111.2 s, 1045.1 s, 1022.4 m, 1008.6 m, 957 w, 932.5 w, 908.8 s, 640 w, 769 m, 735 m, 673 m, 659 w, 640 w, 600 m, 536.6 m, 510 w, 504 w, 443 w, 434 w. UV spectrum, hexane, λ (ε, l cm^{-1} mol^{-1}): 285 (4500), 373 (11500), 393 (13000), 544 (1900), 1008 (8100).

Complex III. Yield 0.20 g, 0.31 mmol, 33%. Found, %: C 66.01; H 8.97; N 2.07; Sn 18.06. Calculated, %: C 65.96; H 8.92; N 2.14; Sn 18.11 $C_{36}H_{58}NO_2Sn$. IR spectrum, ν, cm^{-1}: 9877.4 s, 1562.3 w, 1529.0 m, 1516.5 m, 1441.4 m, 1416.4 m, 1358.1 m, 1316.4 s, 1274.7 w, 1229.2 s, 1184.2 s, 1166.3 s, 1112.3 s, 1042.6 m, 1022.3 w, 1008.8 w, 957.1 w, 932.3 w, 907.6 s, 880.6 w, 851.4 s, 772.7 m, 734.3 m, 707.4 m, 664.7 m, 637.7 m, 604.0 w, 536.5 w, 507.3 w, 462.3 w. UV spectrum, hexane, λ (ε, l cm^{-1} mol^{-1}): 285 (4500), 373 (11500), 393 (13000), 544 (1900), 1008 (8100).

Complex IV. Yield 0.44 g, 0.67 mmol, 71 %. Found, %: C 66.03; H 9.01; N 2.01; Sn 18.03. Calculated, %: C 65.96; H 8.92; N 2.14; Sn 18.11. $C_{36}H_{58}NO_2Sn$. IR spectrum, ν, cm^{-1}: 9877.4 s, 1523.3 m, 1417.5 m, 1360.1 s, 1320.8 s, 1272.5 w, 1233.2 s, 1178.8 s, 1112.4 s, 1042.9 s, 1024.7 m, 1009.6 m, 955.3 w, 931.1 w, 909.9 m, 888.8 w, 846.5 m, 770.9 m, 665.2 w, 641.0 w, 601.7 w, 562.5 w, 535.3 m, 508.1 w. UV spectrum, hexane, λ (ε, l cm^{-1} mol^{-1}): 285 (4200), 375 (9500), 394 (13400), 544 (1900), 1008 (7500).

Complex V. Yield 0.47 g, 0.69 mmol, 73%. Found, %: C 70.04; H 7.37; N 1.89; Sn 17.01. Calculated, %: C 69.07; H 7.25; N 2.01; Sn 17.07 $C_{40}H_{50}NO_2Sn$. IR spectrum, ν, cm^{-1}: 9877.4 s, 1528.9 w, 1522.9 w, 1445.6 s, 1415.9 s, 1360.4 s, 1318.8 s, 1275.2 s, 1174.2 s, 1110.7 s, 1096 w, 1075 w, 1063.2 w, 1043.4 s, 1024.5 m, 1008.7 m, 906.6 s, 851.1 s, 767.9 m, 729.3 s, 696 s, 663.9 m, 638.1 m, 601.4 m, 538 m, 510.3 m, 462.7 w, 449 m, 438 w. UV spectrum, λ (ε, l cm^{-1} mol^{-1}): 284 (5200), 370 (10500), 391 (12900), 552 (2100), 1008 (7500).

Synthesis of complex VI. The reaction was carried out in the absence of air oxygen and moisture. To the solution of dimethyltin(IV) dichloride (Me_2SnCl_2 0.21 g, 0.94 mmol) and bis(2-hydroxy-3,5-di-*tert*-butylphenyl)amine (0.4 g, 0.94 mmol) in 20 ml of acetonitrile 0.26 ml of triethylamine was added. Then, acetonitrile was removed under reduced pressure, the residue was dissolved in *n*-hexane to give white precipitate of $[Et_3NH]Cl$. The reaction mixture was filtered off through a glass frit, the filtrate was cooled to –20°C, the formed precipitate of the tin(IV) complex was separated by decantation to obtain 0.18 g, 0.31 mmol (33%) of complex **VI**. Found, %: C 63.08; H 8.34; N 2.36; Sn 20.21. Calculated, %: C 62.95; H 8.28; N 2.45; Sn 20.74. $C_{30}H_{47}NO_2Sn$. IR spectrum, ν, cm^{-1}: 2758.7 w, 1562.3 w, 1487.3 s, 1416.4 s, 1362.3 s, 1303.9 s, 1262.2 s, 1241.3 s, 1203.8 m, 1162.1 m, 1128.8 m, 995.4 s, 870.3 m, 774.5 m, 753.6 m, 737.0 m, 691.1 w, 670.3 w, 649.4 w, 636.9 w, 607.7 m, 561.9 w, 528.5 m, 507.7 w, 486.9 m. ^1H NMR, δ, ppm, *J*, Hz: 7.02 d (2H, $2CH_{arom}$, 2.0), 6.73 d (2H, $2CH_{arom}$, 2.0), 5.44 s (H, NH), 1.54 s (18H, 2*t*-Bu), 1.25 s [3H, CH_3Sn, $J(H–^{119}Sn)$ 84.22], 1.22 s (18H, 2*t*-Bu), 1.18 s [3H, CH_3Sn, $J(H–^{119}Sn)$ 79.72].

Synthesis of complex VII. 3,5-Di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (0.1 g, 0.24 mmol) reacted with Ph_3PbOH (0.11 g, 0.24 mmol) in 10 ml of methanol, the mixture turned green. The solution was stirred for 2 h, the color changed to violet. The obtained mixture was investigated by the ESR spectroscopy without isolation.

Synthesis of complexes VIII, IX. Me_3SiCl (0.0097 g, 0.09 mmol), Et_3PbCl (0.029 g, 0.09 mmol) reacted

with 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (0.04 g, 0.09 mmol) in hexane in the presence of 0.1 ml of triethylamine. The obtained mixture was investigated by the ESR spectroscopy without isolation.

Synthesis of radical L^0. 3,5-Di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine was shaken with suspension of excess lead(IV) oxide in *n*-hexane in the absence of air oxygen and moisture. The obtained mixture was investigated by the ESR spectroscopy in solution. The compound was not isolated in an individual state.

Synthesis of radical X. 3,5-Di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine reacted with equimolar amount of silver triflate in *n*-hexane in the absence of air oxygen and moisture. The reaction mixture was investigated by the ESR spectroscopy without isolation.

ACKNOWLEDGMENTS

This work was performed with a financial support from the subprogram of Presidium RAS "Design of magnetoactive compounds and materials," Grants of RFBR (nos. 07-03-00711 and 07-03-00819), Grants of the President of RF (nos. NSh 4182.2008.3 and MK 1286.2009.3).

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