ESR investigation of paramagnetic derivatives of [6-*tert*-butyl-4-(5-*tert*-butyl-2-methyl-3,4-dioxocyclohexa-1,5-dien-1-yl)-3-methylcatecholato]triphenylantimony(v)*

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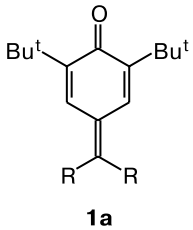
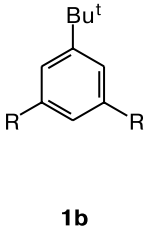
A number of paramagnetic derivatives of [6-*tert*-butyl-4-(5-*tert*-butyl-2-methyl-3,4-dioxocyclohexa-1,5-dien-1-yl)-3-methylcatecholato]triphenylantimony(v) were investigated by ESR spectroscopy. The reactions of this complex with Cp_2Co or LiCl in the presence of $Hg_{metal.}$ lead to the formation of free (nonchelated) radical anion semiquiones. Chelated complexes are formed in the case of Tl(Hg), $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, Sn_2Ph_6, Cu(met.), and CuCl + dppfc (dppfc is bis-diphenylphosphinoferrocene).

Key words: ESR spectroscopy, di-*o*-quinone, *o*-semiquinonato metal complexes, catecholatotriphenylantimony(v).

An important and promising line of research in the chemistry of *o*-semiquinone metal complexes is the study of intramolecular electronic interactions (metal—ligand, metal—metal, ligand—ligand), depending on the molecular geometry and the system behavior. The topicality of the studies in this field is related to the search for new approaches to the design of molecular electronic devices[1—3] and molecular magnets,[4—6] being developed intensively in recent years. Of particular interest in this respect are di-*o*-quinones, able to form bi- and polynuclear complexes with bridging paramagnetic ligands. Their use provides new opportunities for the synthesis of high-spin systems and bi-stable metal complexes. Two types of derivatives of this sort are now known. A series of homometal binuclear di-*o*-semiquinone complexes (**1a,b**) have been reported.[7,8] In these complexes, the ligand exists as so-called "nonalternate biradical" whose structure ensures the ferromagnetic type of the exchange between the radical centers.



1a



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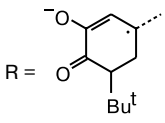
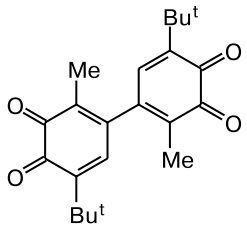


Previously,[9—11] we reported the synthesis and the structures of a number of mono-, bi-, and polynuclear complexes derived from 4,4′-di-(6-*tert*-butyl-3-methylbenzo-1,2-quinone) (**2**). The reduction of **2** may yield three paramagnetic species: radical monoanion, radical dianion, and radical trianion. A number of examples have been reported for the first two species, quinone-semiquinone and di-semiquinone derivatives.[9,10] For the third type, *i.e.*, the catecholato-semiquinone form, only one example is known: the tripotassium salt.[11]

Heteronuclear complexes derived from **2** have not been described until recently. Recently, we obtained, by oxidative addition, quinone catecholate (**3**),[12] which served as the starting synthon for the synthesis of catecholato-semiquinone derivatives.



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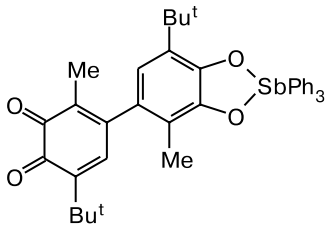

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This communication presents a ESR study of paramagnetic heteronuclear complexes obtained by the reduction of quinone catecholate (**3**).

* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

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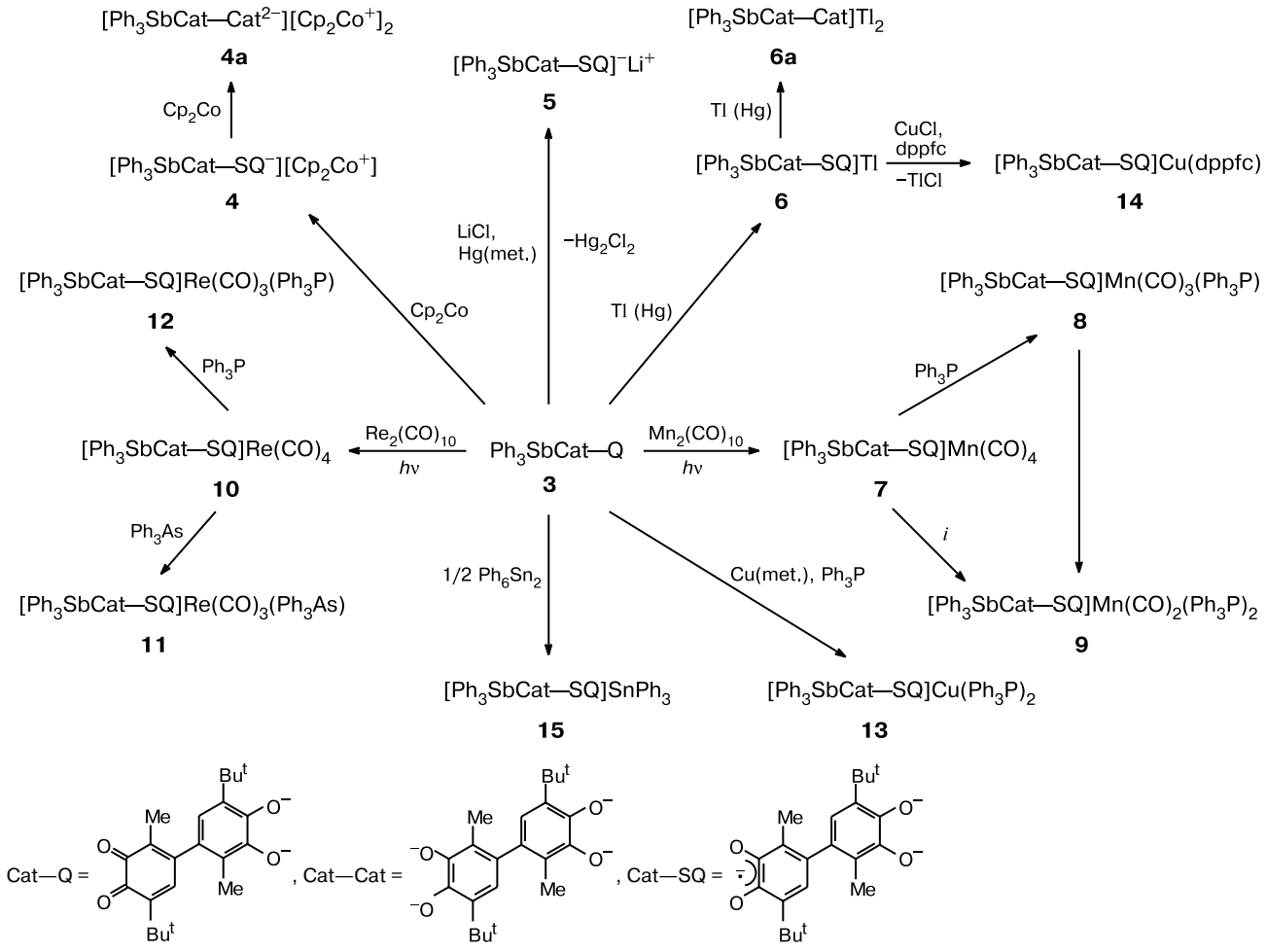
Results and Discussion

The single-electron reduction of complex **3** with cobaltocene in THF (with some deficiency of cobaltocene) gives cobalticinium catechol semiquinolate **4** (Scheme 1). The ESR spectrum of **4** is a doublet with a line width of ~0.15 mT. The doublet is due to the HFC of the unpaired electron with the H(5) proton of the semiquinone fragment with the HFS constant $A_i(H) = 0.36$ mT. The hyperfine coupling with the magnetic nuclei of the cobalticinium cation is missing. The reaction of quinones with cobaltocene results in the formation of free (nonchelated to the metal) semiquinone radical anions, as indicated by the absence of the HFC of the unpaired electron and cobalt magnetic nuclei in the ESR spectra.[13] The subsequent reaction with cobaltocene results in the reduction of **4** to diamagnetic bis-catecholate $[Ph_3SbCat—Cat^{2-}][Cp_2Co^+]_2$ (**4a**) (see Scheme 1).

It is known that *o*-quinones are capable of single-electron reduction with metallic silver, copper, or mercury[14,15] in solvating solvents in the presence of lithium halide. Quinone catecholate **3** is also able to undergo single-electron reduction with metallic mercury in the presence of LiCl (see Scheme 1) in a THF solution. The ESR spectrum of the resulting lithium semiquinolate **5** resembles the ESR spectrum of cobalticinium semiquinolate **4**. The doublet $A_i(H^5) = 0.32$ mT is coupled with the H(5) proton.

The reaction of compound **3** with thallium amalgam affords chelated thallium(I) semiquinolate (**6**), as indicated by splitting on thallium magnetic isotopes (^{203}Tl, $I = 1/2$, 29.52%, $\mu_N = 1.6222$; ^{205}Tl, $I = 1/2$, 70.48%, $\mu_N = 1.6382$).[16] As in the case of thallium(I) *o*-semiquinolates and *o*-iminobenzosemiquinolate reported previously,[17,18] thallium(I) catechol semiquinolate **6** shows a dependence of the HFC constant $A_i(^{203,205}TI)$ on the sol-

Scheme 1



Note. i. Excess Ph_3P. dppfc is bis(diphenylphosphino)ferrocene.

Table 1. Parameters of the isotropic ESR spectra of semiquinone derivatives **4—15** at 290 K

Complex	Structure	Solvent	g_i	A_i(M) (isotope)	$A_i(H^5)$	$A_i(^{31}P)$ or $A_i(^{75}As)$ (isotope)
					mT	
4	$[Ph_3SbCat—SQ]^-[Cp_2Co^+]$	THF	2.0046	—	0.36	—
5	$[Ph_3SbCat—SQ]^-Li^+$	THF	2.0033	—	0.33	—
6	$[Ph_3SbCat—SQ]Tl$	Toluene	1.9964	4.35 (^{203}Tl)	0.35	—
				4.39 (^{205}Tl)		
		THF	1.9974	5.83 (^{203}Tl)		
				5.89 (^{205}Tl)	0.35	—
		Et_3N	1.9981	8.73 (^{203}Tl)		
				8.82 (^{205}Tl)	0.35	—
7	$[Ph_3SbCat—SQ]Mn(CO)_4$	Toluene	2.0039	0.685 (^{55}Mn)	0.34	-
8	$[Ph_3SbCat—SQ]Mn(CO)_3(Ph_3P)$	Toluene	2.0033	0.96 (^{55}Mn)	0.33	3.36 (^{31}P)
9	$[Ph_3SbCat—SQ]Mn(CO)_2(Ph_3P)_2$	Toluene	2.0041	1.79 (^{55}Mn)	0.33	3.94 (^{31}P)
10	$[Ph_3SbCat—SQ]Re(CO)_4$	Toluene	2.0045	2.74 (^{187}Re,^{185}Re)	0.40	—
11	$[Ph_3SbCat—SQ]Re(CO)_3(Ph_3As)$	Et_2O	2.0024	3.32 (^{187}Re,^{185}Re)	0.40	3.39 (^{75}As)
12	$[Ph_3SbCat—SQ]Re(CO)_3(Ph_3P)$	Et_2O	2.0036	3.63 (^{187}Re,^{185}Re)	0.40	2.64 (^{31}P)
13	$[Ph_3SbCat—SQ]Cu(Ph_3P)_2$	THF	2.0050	1.060 (^{63}Cu)	0.30	1.415 (1st P)
				1.135 (^{65}Cu)		1.785 (2nd P)
14	$[Ph_3SbCat—SQ]Cu(dppfc)$	THF	2.0058	1.121 (^{63}Cu)	0.32	1.637 (1st P)
				1.198 (^{65}Cu)		1.855 (2nd P)
15	$[Ph_3SbCat—SQ]SnPh_3$	Toluene	2.0037	0.994 (^{117}Sn)	0.34	—
				1.040 (^{119}Sn)		

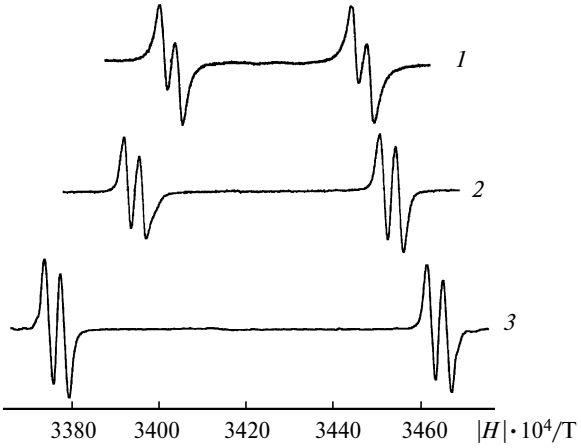
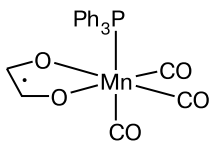


Fig. 1. Isotropic ESR spectra of thallium catechol semiquinolate **6** in toluene (*1*), THF (*2*), triethylamine (*3*) at 290 K.

vent nature (Fig. 1). Parameters of isotropic ESR spectra of complex **6** in some solvents are listed in Table 1. The subsequent reaction with thallium amalgam results in the reduction of thallium semiquinolate **6** to diamagnetic dicatecholate **6a**.

The irradiation of a solution of quinone catecholate **3** with full light of a KGM-24-150 lamp with a focusing device (visible range) in the presence of $Mn_2(CO)_{10}$ yields mono-*o*-semiquinone complex $[Ph_3SbCat—SQ]Mn(CO)_4$ (**7**). The isotropic ESR spectrum of complex **7** exhibits the HFS with the manganese nucleus (^{55}Mn, 100%, $I = 5/2$, $\mu_N = 3.4687$)[16] and with the H(5) proton of the semiquinone ring (Fig. 2, *a*). Treatment with triphenylphosphine results in replacement of the CO group, giving rise to additional splitting on the phosphorus magnetic nucleus (^{31}P, 100%, $I = 1/2$, $\mu_N = 1.13160$)[16] with a constant of 3.36 mT (Fig. 2, *b*). It is noteworthy that due to the anisotropy of the g-tensor, the line intensities in the high-field part of the experimental spectrum of **8** are lower than those in the low-field part. The simulation did not take into account this anisotropy; therefore, the line intensities in the simulated spectrum are equal. The diphosphine derivative $[Ph_3SbCat—SQ]Mn(CO)_2(Ph_3P)_2$ (**9**), whose ESR spectrum is shown in Fig. 2, *c*, is formed on treatment of **7** (or **8**) with an excess of triphenylphosphine. The large values of the HFC constant $A_i(^{31}P)$ for the monophosphine (**8**) and diphosphine (**9**) derivatives (see Table 1) indicate that phosphine ligands occupy the apical positions.[19]



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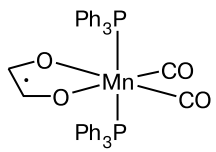

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Simultaneously, the HFS constant with the manganese nucleus $A_i(^{55}Mn)$ increases from 0.685 mT in complex **5** to 0.96 mT in the monophosphine derivative **8** and to 1.79 mT in the diphosphine complex **9**. It is noteworthy that, unlike the semiquinone derivatives $SQMn(CO)_4$

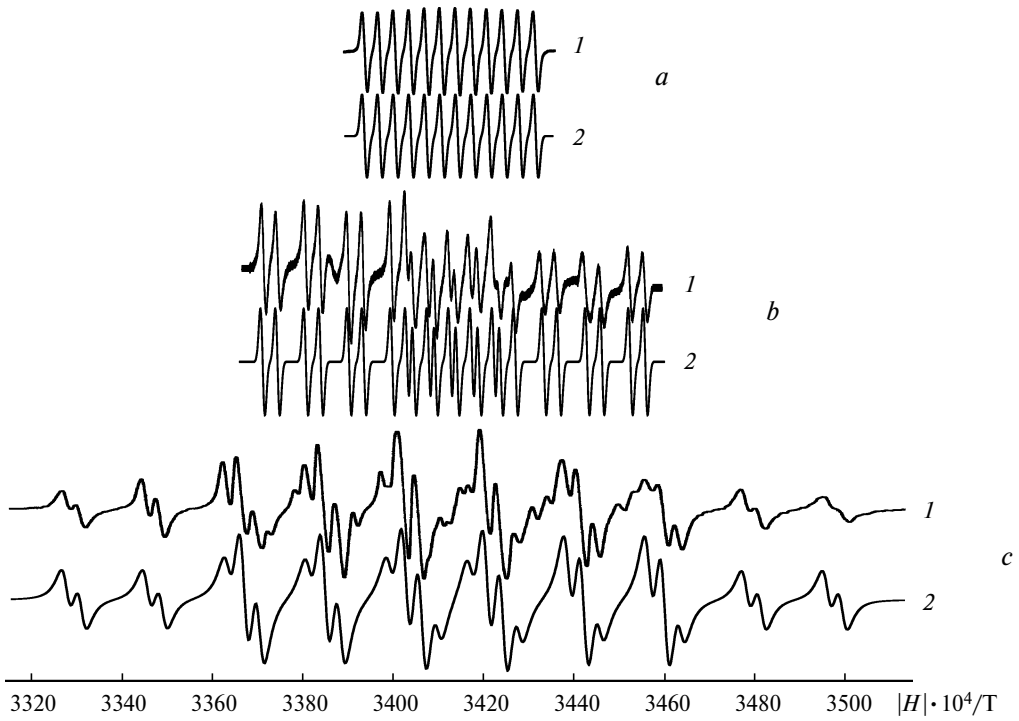
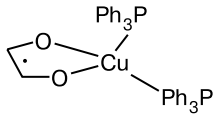


Fig. 2. ESR spectra of derivatives **7** (*a*), **8** (*b*), and **9** (*c*): (*1*) experimental (toluene, 290 K), (*2*) simulated. The additional components in the experimental ESR spectrum **9** refer to the monophosphine complex **8**.

studied previously, in which the replacement of the second CO group by the phosphine is hampered,[20] in the case of complex **7**, this reaction proceeds much more easily.

The irradiation of a solution of quinone catecholate **3** with the full light of a KGM-24-150 lamp with a focusing device (visible region) in the presence of $Re_2(CO)_{10}$ also affords the mono-*o*-semiquinone complex $[Ph_3SbCat—SQ]Re(CO)_4$ (**10**). The ESR spectrum exhibits an HFS with the magnetic isotopes of rhenium (^{187}Re, 62.60%, $I = 5/2$, $\mu_N = 3.2197$; ^{185}Re, 37.40%, $I = 5/2$, $\mu_N = 3.172$)[16] and with the H(5) proton of the semiquinone ring. Treatment of compound **10** with Ph_3P and Ph_3As yields the substitution products **11** and **12**. The spectrum of the substituted complex $[Ph_3SbCat—SQ]Re(CO)_3(Ph_3As)$ (**11**) exhibits an additional splitting on the arsenic magnetic nucleus (^{75}As, 100%, $I = 3/2$, $\mu_N = 1.43947$)[16] with the constant 3.39 mT, while that of the phosphine complex $[Ph_3SbCat—SQ]Re(CO)_3(Ph_3P)$ (**12**), on the ^{31}P magnetic nucleus with a constant of 2.64 mT. For complexes **11** and **12**, the HFS constants $A_i(^{185}Re, ^{187}Re)$ are 3.32 mT and 3.63 mT, respectively, which is similar to the corresponding value, $A_i(^{185}Re, ^{187}Re) = 3.87$ mT, for the rhenium 3,5-di-*tert*-butylbenzosemiquinone complex synthesized previously.[20]

The semiquinone copper complexes with neutral ligands can be obtained in several ways.[21—23] In a solvating solvent in the presence of Ph_3P, the quinone catecholate **3** dissolves metallic copper to give the semiquinolate $[Ph_3SbCat—SQ]Cu(Ph_3P)_2$ (**13**) (see Scheme 1). The ESR spectrum of the resulting complex **13** exhibits an HFC of the unpaired electron with the magnetic isotopes of one copper atom (^{63}Cu, 69.09%, $I = 3/2$, $\mu_N = 2.2206$; ^{65}Cu, 30.91%, $I = 3/2$, $\mu_N = 2.3790$),[16] two ^{31}P nuclei, and the H(5) proton (Fig. 3). The contribution of the methyl-group protons to the HFC is manifested as an increase in the ESR line width. A specific feature of the ESR spectrum is nonequivalence of the HFC constants with phosphorus $A_i(^{31}P)$ (1.415 mT and 1.785 mT), indicating an asymmetric arrangement of the triphenylphosphine ligands with respect to the plane of the semiquinone radical anion.



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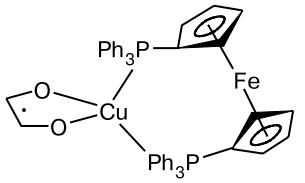
Generally, the HFC constants with the proton and the magnetic isotopes of copper and phosphorus are typical of copper(I) semiquinone complexes.[21]

Another method for the preparation of copper semiquinone complexes is the reaction of a thallium semiquinone salt with copper(I) chloride in the presence of neutral ligands.[22] For example, the reaction of thallium semiquinolate **6** with copper(I) chloride in the presence of



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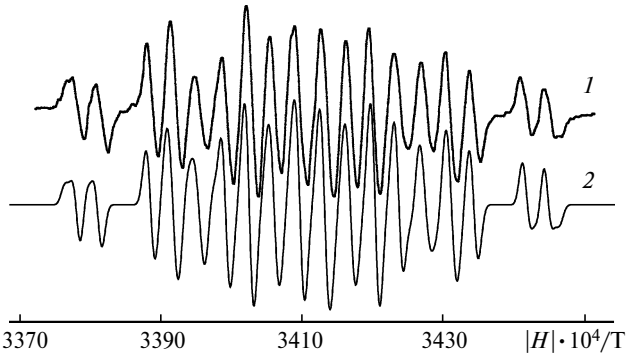

Fig. 3. ESR spectrum of the copper complex **13** $[Ph_3SbCat—SQ]Cu(Ph_3P)_2$: (*1*) experimental (toluene, 290 K), (*2*) simulated.

dppfc (see Scheme 1) gave the copper(I) semiquinone complex $[Ph_3SbCat—SQ]Cu(dppfc)$ (**14**).

The ESR spectrum of derivative **14** also reflects an HFC with the magnetic nuclei of two nonequivalent phosphorus atoms (1.637 and 1.855 mT), the magnetic isotopes of one copper atom, and the H(5) proton (Fig. 4). The ESR parameters of copper complexes **13** and **14** are summarized in Table 1.

The reaction of hexaphenyldistannane with quinone catecholate **3** in a molar ratio of 1 : 2 gave the complex $[Ph_3SbCat—SQ]SnPh_3$ (**15**), whose ESR spectrum (Fig. 5) is a doublet of multiplets with satellites caused by the HFC of the unpaired electron with the magnetic isotopes

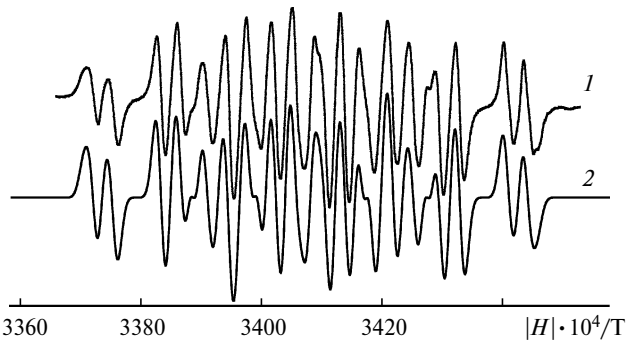

Fig. 4. ESR spectrum of the copper complex **14** $[Ph_3SbCat—SQ]Cu(dppfc)$: (*1*) experimental (toluene, 290 K), (*2*) simulated.

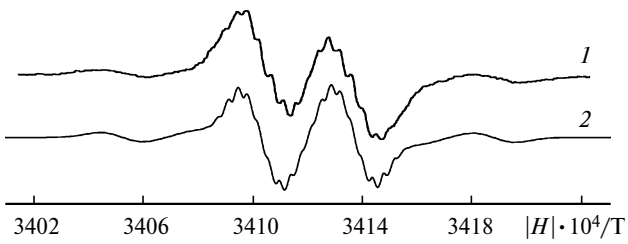

Fig. 5. ESR spectrum of the complex $[Ph_3SbCat—SQ]SnPh_3$ (**15**): (*1*) experimental (toluene, 290 K), (*2*) simulated.

of one tin atom (^{117}Sn, 7.75%, $I = 1/2$, $\mu_N = 1.000$; ^{119}Sn, 8.60%, $I = 1/2$, $\mu_N = 1.046$).[16] The doublet of multiplets is related to the HFC of the unpaired electron with the H(5) proton (0.34 T) and with the protons of the 3- and 3′-methyl groups (0.04 T).

Experimental

The solvents were purified and dehydrated by standard procedures.[24] [6-*tert*-Butyl-4-(5-*tert*-butyl-2-methyl-3,4-dioxocyclohexa-1,5-dien-1-yl)-3-methylcatecholato]triphenylantimony(v) was prepared by a previously described method.[12]

The ESR spectra were recorded on a Bruker ER 200 D-SRC spectrometer equipped with a ER 4105 DR double cavity and ER 4111 VT thermal controller. The spectra were simulated using the WinEPR SimFonia v1.25 program (Bruker). The *g*-factors were determined using diphenylpicrylhydrazyl as the standard. The parameters of the ESR spectra of complexes **4—15** obtained in this way are presented in Table 1.

All experiments on the synthesis of complexes **4—15**, including **4a** and **6a**, were carried out in evacuated tubes in the absence of oxygen or water traces at 290 K using solvents indicated in Table 1. The resulting compounds were not isolated in a pure state. The complexes $[Ph_3SbCat—SQ]Mn(CO)_4$ (**7**) and $[Ph_3SbCat—SQ]Re(CO)_4$ (**10**) were prepared by irradiating solutions of $Ph_3SbCat—SQ$ (**3**) in toluene for 3 min with the full light of a KGM-24-150 lamp with a focusing device (visible range) in the presence of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively.

The reduction of complex **3** with cobaltocene in THF to cobalticinium catechol semiquinolate **4** was conducted at a complex **3** to cobaltocene molar ratio of 1.5 : 1.

The complex $[Ph_3SbCat—SQ]Mn(CO)_3(Ph_3P)$ (**8**) was prepared by treatment of the mono-*o*-semiquinone complex $[Ph_3SbCat—SQ]Mn(CO)_4$ (**7**) with triphenylphosphine taken in an equimolar ratio.

The complex $[Ph_3SbCat—SQ]SnPh_3$ (**15**) was prepared by the reaction of hexaphenyldistannane with quinone catecholate **3** in a 1 : 2 molar ratio.

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