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Synthesis and ESR spectra of [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinonato]thallium(I)*

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[4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinonato]thallium(I) was synthesized and characterized by IR and ESR spectroscopy. The hyperfine coupling constants with $^{203/205}$Tl nuclei were found to depend strongly on the nature (solvating ability) of solvents. At 298 K, the HFC constant a_{Tl} changes from 3.09 mT in *n*-hexane up to 19.70 mT in tetramethylethylenediamine. The coordination number of solvation was found to be 1 for DMF—benzene and pyridine—hexane systems. The thermodynamic characteristics of solvation in the pyridine—hexane system were determined.

Key words: solvation, ESR spectroscopy, *o*-iminobenzoquinone, thallium.

ESR spectroscopy of metal complexes is an efficient method for studying the dynamics of fast low-energy processes in the coordination sphere of complexes. For instance, the kinetic phenomenon of the so-called "wandering valence" was found and characterized[1] in detail for *o*-semiquinone complexes of III—V Group elements. The thermodynamic and kinetic parameters of redox isomerism of *o*-semiquinone complexes of transition metals were obtained by studying the temperature plots of the ESR spectra of the rhodium, iridium, and copper complexes.[2—4] Several phenomena were found for the copper *o*-semiquinone complexes: reversible intramolecular metal—ligand electron transfer induced by ligand substitution,[5] solvatoisomerism,[6] and isomerization of the stoichiometrically non-rigid copper(I) complexes.[7] Thallium(I) *o*-semiquinone complexes are characterized by a unique sensitivity of parameters of the ESR spectra to the solvent nature.[8]

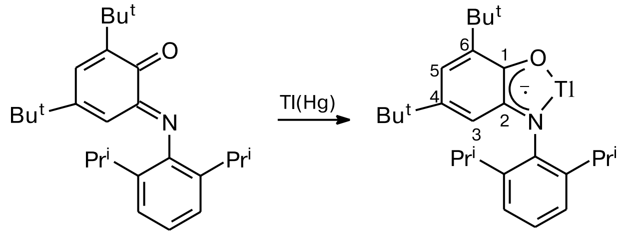
The chemistry and ESR spectroscopy of *o*-iminobenzosemiquinones, which are the closest analogs of *o*-semiquinones, were not developed up to date to such an extent as those for their analogs. Several *o*-iminosemiquinone complexes of transition metals, which demonstrate high similarity to the *o*-semiquinone derivatives, have recently been synthesized.[9,10]

In this work, we synthesized [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinonato]thallium(I) and studied its ESR spectral parameters as functions of the solvent nature and temperature.

Results and Discussion

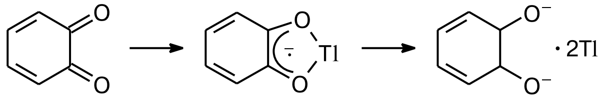
We found that the reduction of *o*-iminobenzoquinone (**1**) with thallium almalgam (Scheme 1) affords [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinonato]thallium(I) (**2**).

Scheme 1



1 **2**

As shown in earlier study[11] of thallium *o*-semiquinone complexes, the prolonged reduction of benzoquinone with thallium amalgam transforms the intermediate *o*-benzosemiquinone radical anion to the catecholate dianion.



Unlike this, thallium(I) *o*-iminobenzosemiquinone (**2**) is not reduced in the presence of thallium amalgam.

Complex **2** was isolated in the individual state and characterized by the data of IR spectroscopy, ESR spectroscopy, and elemental analysis.

The presence of the iminobenzoquinone ligand in the complex is indicated by a characteristic set of bands in a region of 700—1600 cm^{-1}. The reduction of *o*-iminobenzoquinone is confirmed by the absence of characteristic bands of stretching vibrations of the C=O and C=N

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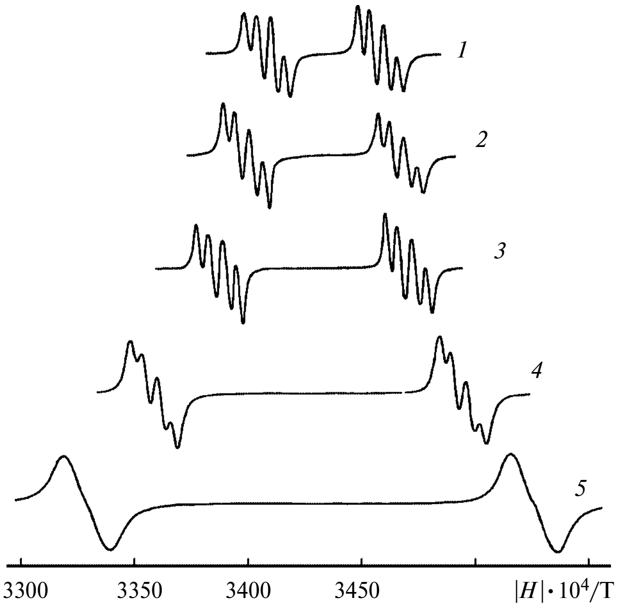


Fig. 1. ESR spectra of complex **2** in solutions of methylene dichloride (*1*), diethyl ether (*2*), THF (*3*), pyridine (*4*), and TMEDA (*5*) at 290 K.

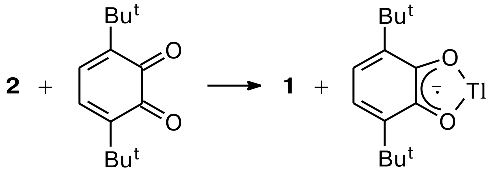
bonds of *o*-iminobenzosemiquinone (1670 and 1635 cm^{-1}, respectively) in the IR spectrum.

The complex is paramagnetic in both the solid state and solution. The ESR spectrum of a polycrystalline sample of the complex is typical of systems with two unpaired electrons, indicating the dimeric structure of the complex in the solid state. The splitting parameter in the zero field is $D_{\|} = 75.6$ mT. This value allows one to calculate the average distance between the radical centers r, which is equal to 4.2 Å. Solutions of the complex exhibit the isotropic ESR spectrum: a doublet of quartets (Fig. 1). The hyperfine structure of the spectrum is caused by the hyperfine coupling of an unpaired electron with the magnetic isotopes (^{203}Tl, I = 1/2, 29.52%, μ_N = 1.6222; ^{205}Tl, I = 1/2, 70.48%, μ_N = 1.6382)[12] of one thallium atom, the nitrogen atom (^{14}N, I = 1, a_N(1 N) = 0.66 mT), and the proton ($a_{H(5)}$(1 H) = 0.48 mT) of the iminoquinone fragment. The coupling on the second proton of the iminoquinone fragment (H(3)) is low compared to the linewidth.

Complex **2** is highly sensitive to oxygen in both solution and the solid state. In the absence of oxygen and moisture, it can be stored for a long time without noticeable decomposition.

The ESR study showed that the complex undergoes redox reactions with *o*-quinones followed and displacement of free *o*-iminobenzoquinone.

In the ESR spectrum, the doublet of quartets from the *o*-iminobenzosemiquinonatothallium complex disappears, and a doublet of triplets (1 : 2 : 1) appears, which is caused by the HFC of the unpaired electron with the thallium nucleus and two equivalent protons in positions 4 and 5 of *o*-semiquinone **3**.



3 **4**

As in the case of the thallium(I) *o*-semiquinone complexes, the parameters of the isotropic ESR spectra (g and a_{Tl}) depend very strongly on the solvent nature and temperature.

At room temperature (290 K), the HFC constant a_{Tl} in the ESR spectrum of the complex changes from 3.09 mT in hexane to 19.70 mT in tetramethylethylenediamine (TMEDA) (see Fig. 1), while the HFC constants with magnetic nuclei of the ligand remain unchanged. This indicates that the spin density distribution between the metal and ligand remains unchanged. The g factors also demonstrate a tendency of increasing with an increase in the donor ability of the solvent. The a_{Tl} and g values are presented in Table 1.

The temperature plots of the HFC constants a_{Tl} and g factors for complex **2** in different solvents are presented in Fig. 2. As a whole, despite some deviations, a tendency of increasing both the HFC constants a_{Tl} and g factors with the temperature decrease is observed.

The study of the thallium HFC constants in a mixture of two solvents, solvating and unsolvating (under assumption that hexane is incapable of specific solvation[8]) makes it possible to determine the coordination number of sol-

Table 1. Parameters of the ESR spectra for complex **2** in different solvents at 290 K

Solvent	a/mT	g
TMEDA	19.70	1.9962
Piperidine	15.47	1.9968
Pyridine	13.59	1.9969
DMSO	12.06	1.9959
Triethylamine	11.79	1.9942
DMF	10.09	1.9955
Dimethoxyethane	9.36	1.9948
THF	8.31	1.9951
Dioxane	7.80	1.9950
Ethyl acetate	7.19	1.9940
Acetonitrile	6.88	1.9934
Et$_2$O	6.81	1.9925
Toluene	5.28	1.9927
Benzene	5.21	1.9928
CH$_2$Cl$_2$	4.97	1.9922
Chloroform	4.62	1.9918
n-Hexane	3.09	1.9910

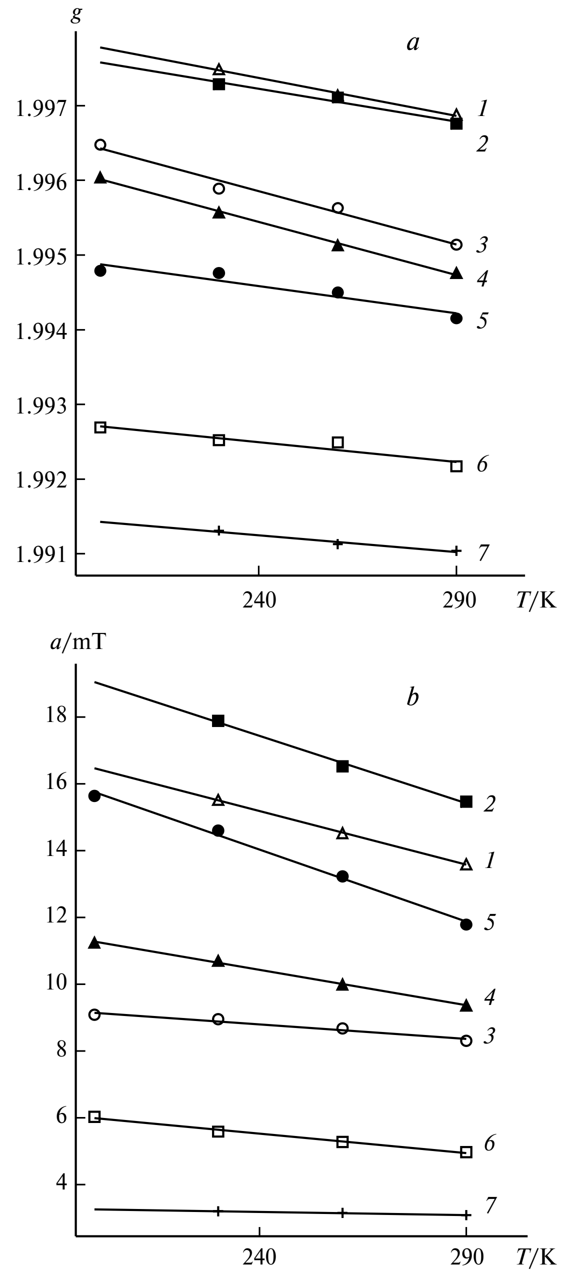


Fig. 2. Temperature plots of the (*a*) *g* factors and (*b*) HFC constants a_{Tl} for complex **2** in different solvents: *1*, pyridine; *2*, piperidine; *3*, THF; *4*, DMF; *5*, triethylamine; *6*, CH_2Cl_2; and *7*, *n*-hexane.

vation *n* and the equilibrium constant of solvation *K* in Eq. (1)

$$\mathrm{TlL} + n\mathrm{S} \rightleftharpoons \mathrm{TlL}\cdot n\mathrm{S}, \qquad (1)$$

where L is the ligand, and S is the solvent.

The study of the temperature plot of the equilibrium constant gives the thermodynamic characteristics of solvation.

In most cases, a fast exchange between the solvated and unsolvated species occurs in system (1). When the concentration of the solvating solvent or the temperature change, the current HFC constant with the thallium nucleus varies continuously during the fast exchange: $\bar{a} = a_{\mathrm{solv}}p_{\mathrm{solv}} + a_{\mathrm{unsolv}}p_{\mathrm{unsolv}}$, where a_{solv} and a_{unsolv} are the HFC constants a_{Tl} of the solvated and unsolvated forms, respectively; p_{solv} and p_{unsolv} are their molar fractions in the system. The slow exchange was detected for the TMEDA—benzene (2.5% TMEDA), piperidine—hexane (0.2% piperidine), and pyridine—hexane (0.1% pyridine, 200 K) systems. For slow exchange, the ESR spectra exhibit a superposition of the spectra of both solvated and unsolvated species.

The coordination number of solvation *n* equal to unity was found for the DMF—benzene mixture at room temperature.

For the pyridine—hexane mixture, the coordination number of solvation *n* remains equal to unity when the temperature decreases from 320 to 240 K.

The pyridine—hexane system also demonstrates the fast exchange (lifetime of different species is $\tau < 10^{-8}$ s). Based on the ESR spectra, the HFC constant increases with the temperature decrease (Fig. 3). The equilibrium constant in the pyridine—hexane mixture at 300 K is 10.74 L mol^{-1}. The enthalpy of solvation, ΔH_{solv}, is -7.1 ± 0.5 kcal mol^{-1}, and the entropy of solvation, ΔS_{solv}, is -20 cal $(\mathrm{mol\ K})^{-1}$.

As a whole, the phenomenon observed is similar to that found previously[8] for thallium *o*-semiquinolates. The

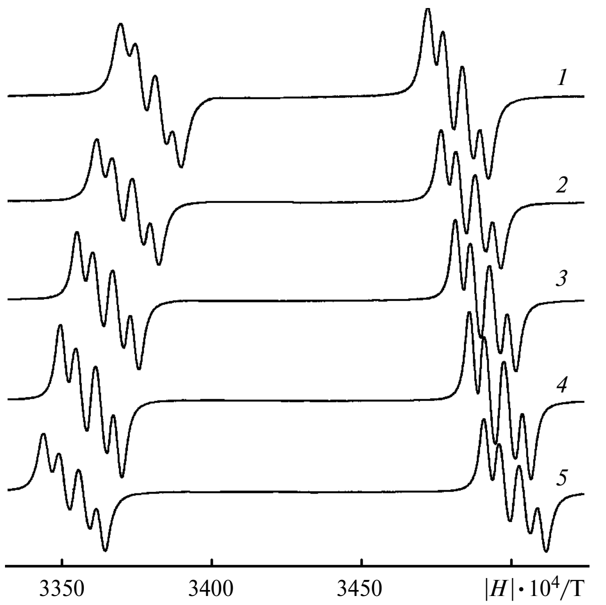


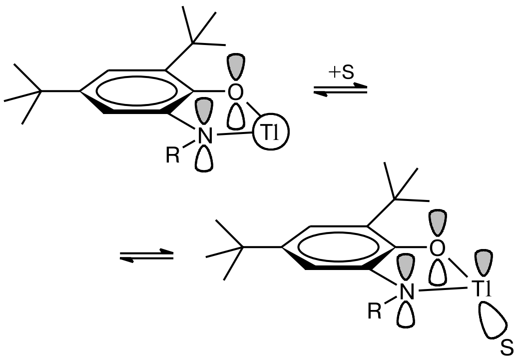
Fig. 3. Changes in the HFC constant a_{Tl} in the pyridine—hexane system (pyridine concentration 0.621 mol L^{-1}) at different temperatures (fast exchange): *1*, 320; *2*, 300; *3*, 280; *4*, 260; and *5*, 240 °C.

authors[8] attributed the changes in a_{Tl} during the solvation of the complex to a change in the geometry and the energy of orbitals in the solvate, resulting in a change in the contribution of the p-AO of thallium to the MO of an unpaired electron.

Two mechanisms of the spin density transfer to the metal are possible[13]: (i) spin polarization of σ-bonds with the metal; (ii) direct interaction of the MO occupied by an unpaired electron through the p-orbitals of oxygen and nitrogen atoms with an energy- and symmetry-appropriate orbital of the metal.

Taking into account the mechanism proposed in Ref. 8, one can assume that the solvation is accompanied by the hybridization of the occupied 6s- and unoccupied 6p-orbitals of thallium to form a tetrahedral coordination sphere (Scheme 2). The vertices of the tetrahedron are occupied by the oxygen and nitrogen atoms at one side and by the solvent molecule (its lone electron pair) and the lone electron pair of thallium at another side. A substantial admixture of the s-orbital, which has a non-zero density on the metal nucleus, appears in the orbitals capable of direct interacting with the orbital of the unpaired electron. This results in the appearance of an additional great contribution to the HFC without changing the spin density in the ligand.

Scheme 2



Thus, it is found that the HFC constant a_{Tl} for [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzosemiquinonato]thallium(I) depends strongly on the solvent nature and temperature. The HFC constant a_{Tl} changes considerably without the spin density redistribution over the metal and ligand, which can be related to a change in the contribution of the s-orbital to the orbital of the metal capable of direct interacting with the MO of an unpaired electron. The coordination number of solvation for DMF—benzene (at 290 K) and pyridine—hexane mixtures (in the temperature interval from 320 to 240 K) was found to be unity.

Experimental

All experiments on the synthesis and the study of properties of [4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl))-*o*-iminobenzosemiquinonato]thallium(I) were carried out in evacuated ampules in the absence of oxygen and water traces.

IR spectra were recorded on a Specord M-80 instrument in Nujol. ESR spectra were obtained on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT thermocontroller.

Solvents were purified and dehydrated according to standard procedures.[14] 4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone was synthesized according to a previously described procedure.[15]

[4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinonato]thallium(I) (2). A solution of **1** (0.758 g, 2 mmol) in THF (35 mL) was added to thallium amalgam in an evacuated ampule. The reaction mixture was vigorously shaken until a dark green solution was obtained. The solution was carefully decanted, and the amalgam was several timed washed with the solvent. Tetrahydrofuran was replaced by toluene (~35 mL), and the solution was concentrated and left in cold. The resulting crystals were filtered off, washed with cold toluene, and dried *in vacuo*. Complex **1** is crystallized as dark green crystals and rapidly decomposes in the presence of oxygen and water traces. It is soluble in polar solvents (TMEDA, pyridine, piperidine, DMF, THF, CH_2Cl_2, Et_2O, *etc.*) and poorly soluble in nonpolar solvents (hexane, CCl_4). The yield was 0.9 g (76.5%). Found (%): C, 53.50; H, 6.81; Tl, 35.5. $C_{26}H_{37}ONTl$. Calculated (%): C, 53.48; H, 6.39; Tl, 35.0. IR (Nujol), ν/cm^{-1}: 1590 w, 1550 m, 1420 vs, 1395 m, 1370 m, 1320 s, 1300 m, 1255 vs, 1240 s, 1195 m, 1170 w, 1125 w, 1105 w, 940 w, 910 w, 850 w, 825 w, 795 m, 730 m, 695 w.

Determination of the coordination number, equilibrium constant, and thermodynamic characteristics of solvation for complex 2. If the condition of fast exchange ($\tau \ll (a_{unsolv} - a_{solv})^{-1}$) is fulfilled, one should observe an averaged spectrum with the HFC constant $\bar{a} = a_{solv}p_{solv}+a_{unsolv}p_{unsolv}$, where a_{unsolv} and a_{solv} are the HFC constants of the unsolvated ($R^{\bullet}$) and solvated ($R^{\bullet}\cdot nS$) forms of the radical, and p_{unsolv} and p_{solv} are the molar fractions of the $R^{\bullet}$ and $R^{\bullet}\cdot nS$ species, respectively. Then $(\bar{a} - a_{unsolv})/(a_{solv} - \bar{a})$ ratio characterizes the ratio of molar fractions of the solvated and unsolvated forms. A linear plot of $(\bar{a} - a_{unsolv})/(a_{solv} - \bar{a})$ *vs.* concentration of a solvent capable of specific solvation suggests one to believe that the coordination number n to be unity.[8]

The plot of ρ *vs.* concentration of the solvating solvent, where $\rho = [(\bar{a} - a_{unsolv})/(a_{solv} - \bar{a}) - 1]/[(\bar{a} - a_{unsolv})/(a_{solv} - \bar{a}) + 1]$, at $\rho = 0$ makes it possible to determine the equilibrium concentration $[S]^{\circ}$, which is related to the equilibrium constant as follows: $[S]^{\circ} = (K)^{-1/n}$. When $n = 1$, then $[S]^{\circ} = 1/K$.[8]

The coupling constants a_{Tl} were measured for DMF—benzene and pyridine—hexane mixtures. A weighed sample of complex **2** was placed in a pre-evacuated ampule with a solded ESR tube, and necessary amounts of both solvents were added. The total volume of the solution was ~2 mL. The system was thoroughly shaken, then a portion of the solution was transferred into the tube, thermostatted, and the ESR spectrum of the solution was recorded.

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