o-Semiquinone metal complexes as derivatives of sterically hindered di-*o*-quinone

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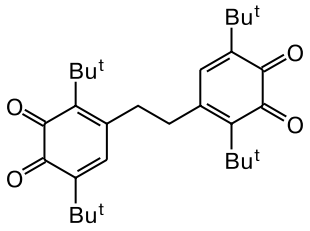
ESR spectroscopy was used to study a series of mono- and binuclear *o*-semiquinone metal complexes, *viz.*, derivatives of sterically hindered di-*o*-quinone 1,2-bis(2,5-di-*tert*-butylcyclohexadiene-1,5-dion-3,4-yl)ethane (**1**). Hindered rotation was found in the *o*-semiquinone moiety of the generated complexes. Magnetochemical measurements for polymeric bis(*o*-semiquinolate)copper(II) based on di-*o*-quinone **1** showed two antiferromagnetic channels of interaction between the paramagnetic centers.

Key words: di-*o*-quinone; *o*-semiquinone complexes of copper, lithium, sodium, potassium, cobalt, manganese; ESR; magnetochemistry.

Studies of metal complexes with high-spin organic ligands is a priority avenue of modern magnetochemistry.[1,2] Among promising ligands, di-*o*-quinones[3—6] play a special role because they can form polynuclear high-spin molecules and also can change magnetic and electronic properties of the synthesized compounds by external factors due to the redox isomerism.[7] In this work, we studied *o*-semiquinone metal complexes, *viz.*, derivatives of sterically hindered di-*o*-quinone 1,2-bis(2,5-di-*tert*-butylcyclohexadiene-1,5-dion-3,4-yl)ethane (**1**).



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Experimental

ESR spectra were recorded on a Bruker-ER-200D-SRC radiospectrometer (working frequency ~9.5 GHz) with an ER-4111VT thermostat. Diphenylpicrylhydrazyl (g = 2.0037) was used as standard for determination of the g factor. Magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design) in the 2—300 K temperature interval in a magnetic field of 0.5 T. The additive diamagnetic contribution of ions was taken into account according to the Pascal constants in calculations of the paramagnetic component of magnetic susceptibility of a complex (χ). The effective magnetic moment as a function of temperature was calculated by the formula

$$\mu_{eff}(T) = [(3k/N\beta^2)\cdot\chi T]^{1/2} \approx (8\chi T)^{1/2},$$

where N is Avogadro´s number, k is the Boltzmann constant, and β is the Bohr magneton.

Di-*o*-quinone **1** was synthesized according to a previously described[8] procedure. Mono- and bis-*o*-semiquinone metal complexes **2—15** based on di-*o*-quinone **1** were generated in solutions according to generally accepted methods.[9—11]

Poly[bis(3,6-di-*tert*-butyl-1,2-semiquinolate)copper] (16). Copper chips (2 g) were added to a solution of di-*o*-quinone **1** (0.3 g) in THF (30 mL) and stirred for 3 days under inert atmosphere. The resulting dark blue suspension was decanted from excess metal and washed with hexane. Blue powdered polymer $[Cu(SQ\text{-}SQ)]_n$ (SQ is 3,6-di-*tert*-butyl-*o*-benzosemiquinone) was obtained in 85% yield (0.289 g). The compound is insoluble in hydrocarbons, ethers, and water. Calculated (%): C, 67.53; H, 7.93; Cu, 12.07. $C_{30}H_{42}O_4Cu$. Found (%): C, 67.91; H, 8.03; Cu, 12.34.

Results and Discussion

At the first stage of the study, mononuclear derivatives of di-*o*-quinone **1**, *viz.*, radical anion salts **2—5** and *o*-semiquinone complexes **6—11**, were generated in solution and studied by ESR spectroscopy. Parameters of the ESR spectra are presented in Table 1.

The room-temperature ESR spectrum of radical-anion complexes **4** and **5**, which were synthesized by the reduction of di-*o*-quinone **1** with metallic potassium or cobaltocene, is a doublet of triplets caused by the interac-

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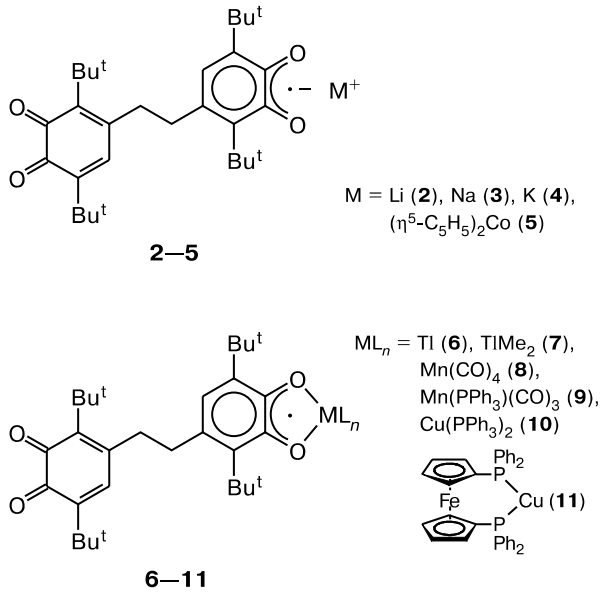


tion of an unpaired electron with a proton of the *o*-semiquinone ring and two protons of the nearest methylene group. The ESR spectra of complexes **2** and **3** contain an additional splitting related to the hyperfine coupling (HFC) of an unpaired electron with the magnetic nuclei ^{7}Li (92.57%, $I = 3/2$, $\mu_N = 3.2560$) and ^{23}Na (100.0%, $I = 3/2$, $\mu_N = 2.2161$).[12] Spin density delocalization is not observed in the second *o*-quinone moiety. The line intensity in the triplet differs from the 1 : 2 : 1 ratio, and its central component is considerably broadened and further broadens with a temperature decrease. At 200 K, the central component is split into two lines (Fig. 1). The observed transformation is caused by hindered rotation about the C—C bond connecting the *o*-semiquinone moiety

Table 1. Parameters of the ESR spectra of the mononuclear metal complexes of di-*o*-quinone **1**

Complex	Solvent	a_i(H)	a_i(2 H)	a_i(M) and a_i(L)	g_i
			mT		
2	THF	0.35	0.19	$a_i(^{7}\text{Li})$ 0.075	2.0039
3	THF	0.35	0.20	$a_i(^{23}\text{Na})$ 0.05	2.0039
4	THF	0.35	0.20	—	2.0037
5	THF	0.36	0.21	—	2.0041
6	THF	0.35	0.21	$a_i(^{203,205}\text{Tl})$ 6.09	1.9961
7	Et_2O	0.36	0.21	$a_i(^{203,205}\text{Tl})$ 3.42	2.0025
8	Toluene	0.33	0.21	$a_i(^{55}\text{Mn})$ 0.72	2.0040
9	Toluene	0.31	0.23, 0.16	$a_i(^{55}\text{Mn})$ 0.98, $a_i(^{31}\text{P})$ 3.48	2.0035
10	Toluene	0.33	0.20	$a_i(^{63}\text{Cu})$ 1.11, $a_i(^{65}\text{Cu})$ 1.18, $a_i(^{31}\text{P})$ 1.69	2.0055
11	Toluene	0.32	0.20	$a_i(^{63}\text{Cu})$ 1.17, $a_i(^{65}\text{Cu})$ 1.25, $a_i(^{31}\text{P})$ 1.89	2.0054

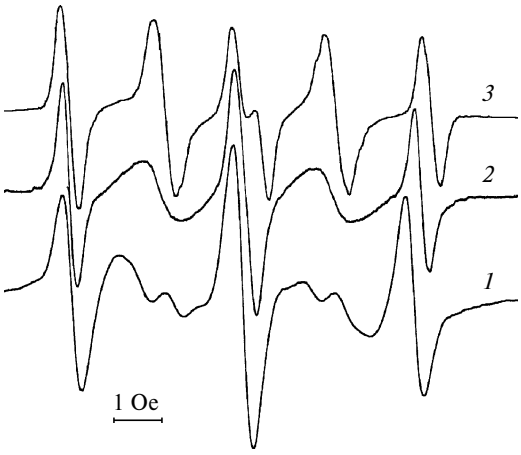


Fig. 1. ESR spectra of di-*o*-quinone radical anion **1** at different temperatures: 200 (*1*), 230 (*2*), and 280 K (*3*).

with the remaining part of the molecule: CH_2CH_2Q (Q is 3,6-di-*tert*-butyl-*o*-benzoquinone). Due to this, protons of the methylene group are nonequivalent in the ESR time scale.

Based on the known ratio between the linewidth at fast exchange and its frequency[13]

$$\nu = \gamma_e(\Delta H)^2/8\pi\Delta\Gamma$$

(ν is the exchange frequency, γ_e is the gyromagnetic ratio for electron, $\Delta\Gamma$ is the contribution to the linewidth from the exchange, and $(\Delta H)^2$ is the squared distance between the exchanging lines in Oe), we determined the rotation frequency in the *o*-semiquinone radical anion at different temperatures. Using the plot of lnν *vs.* $1/T$, we calculated the activation parameters of this process

$$\Delta H^{\neq} = (5.4\pm1.8) \text{ kJ mol}^{-1},$$

$$\Delta S^{\neq} = -(66\pm8) \text{ J mol}^{-1} \text{ K}^{-1}.$$

The temperature at which the protons of the methylene group become nonequivalent in the ESR time scale can serve for the qualitative estimation of the rotation rate. Operating with this magnitude, we can assert that the ligand environment of the central atom in the *o*-semiquinone complexes exerts a substantial effect on the rate of the above-described process. This is well seen for manganese derivatives **8** and **9**. The presence of the bulky triphenylphoshine ligand in the coordination sphere of manganese in complex **9** so impedes rotation that the protons of the CH_2 group are nonequivalent in the ESR spectrum already at 300 K. At the same time, for compound **8** these changes are observed only at 220 K.

Considerable steric hindrance in position 4 of the ring of the *o*-semiquinone moiety substantially affects the coordination sphere of the metal bound to this moiety.

The ESR spectrum of copper phosphine complexes **10** and **11** exhibits HFC of an unpaired electron with the

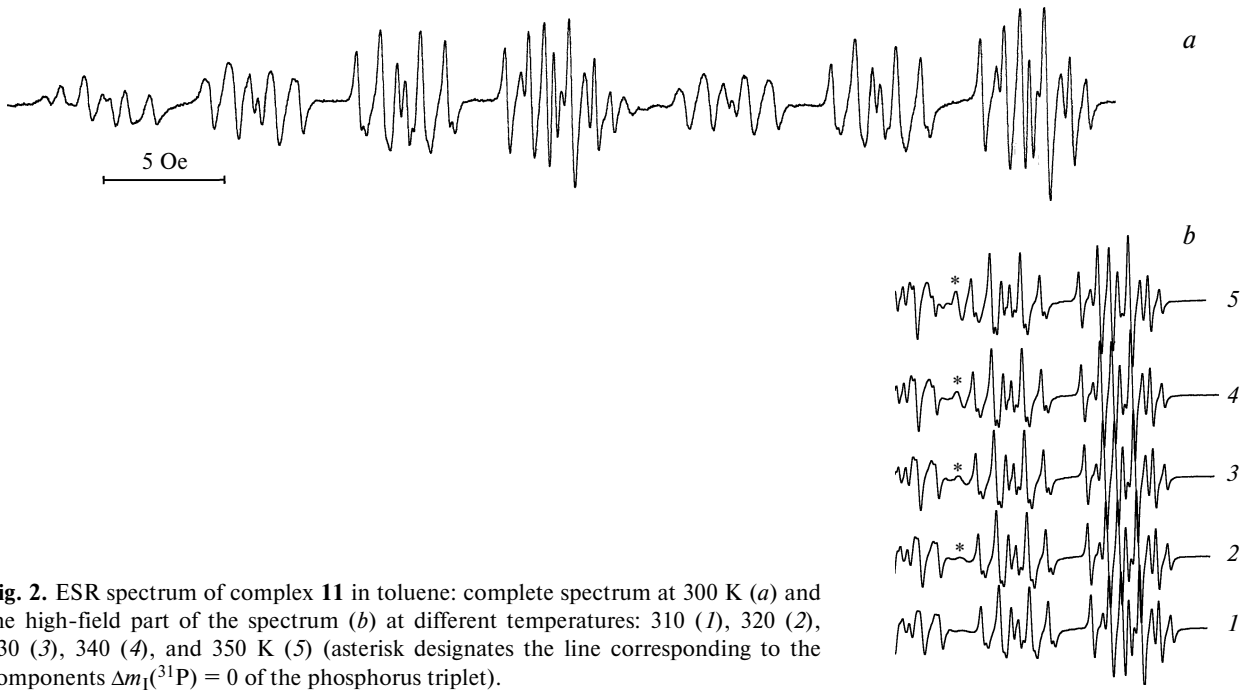


Fig. 2. ESR spectrum of complex **11** in toluene: complete spectrum at 300 K (*a*) and the high-field part of the spectrum (*b*) at different temperatures: 310 (*1*), 320 (*2*), 330 (*3*), 340 (*4*), and 350 K (*5*) (asterisk designates the line corresponding to the components $\Delta m_I(^{31}P) = 0$ of the phosphorus triplet).

proton of the *o*-semiquinone ring, magnetic isotopes of the copper atom, and two phosphorus atoms (Fig. 2, *a*, *b*). However, the intensity distribution of components in the triplet for two equivalent ^{31}P nuclei ($I = 1/2$) differs from the theoretical distribution (1 : 2 : 1). At room temperature, only the components corresponding to the transitions $\Delta m_s(^{31}P) = \pm 1$ are observed (see Fig. 2, *a*). The components $\Delta m_I(^{31}P) = 0$ are substantially broadened, their intensity at 300 K is equal to zero, and they begin to manifest themselves only with the temperature increase (see Fig. 2, *b*). This effect is due, most likely, to slow (in the ESR time scale) exchange of the phosphine ligands between the apical and equatorial positions in the coordination sphere of copper. For some rate of this exchange, the intensity of the central component of the phosphorus triplet can be zero. The temperature increase accelerates this process, which induces averaging of the HFC constants with two phosphorus nuclei and increases the intensity of components corresponding to the transition $\Delta m_I(^{31}P) = 0$. A similar phenomenon was found for the copper(I) *o*-semiquinone complexes with different phosphine ligands, *e.g.*, sterically hindered mono-*o*-quinones.[14] However, this phenomenon was observed only at ~200 K.

Reversible dissociation of the phosphine ligands could also explain this effects. In this case, the ESR spectrum of complex **10** at room temperature should be interpreted as belonging to a complex with the tricoordinate copper atom and one phosphine ligand, which is observed sometimes for compounds of this type.[10] However, in this case, the HFC constant on the ^{31}P phosphorus nucleus should be 0—0.5 mT, which is inconsistent with the values observed for compounds **10** and **11**. In addition, complex **11** with the bidentate phosphine ligand (bis(diphenylphosphino)ferrocene) is not characteristic of the formation of tricoordinate copper(I) *o*-semiquinolates.[15] According to the aforesaid, reversible dissociation of the phosphine ligands for **10** and **11** seems improbable.

Dianionic derivatives of di-*o*-quinone **1** are biradical compounds. The ESR spectra of complexes **12—15** in the frozen solvent matrix are a superposition of a singlet and signals characteristic of triplet species (Fig. 3).

The average distances between the radical centers calculated from the *D* parameter in the approximation of point dipoles[16] for biradicals **12—15** (Table 2) range from 7.2 to 8.2 Å. According to the expected geometry, the resulting values correspond to a esclipsed conformation with a dihedral angle between the *o*-semiquinone moieties of ~120°.

The synthesis of the first polymeric bis(*o*-semiquinolate)copper(II) from di-*o*-quinone of the diphenyl series was reported.[4] We synthesized a similar complex from

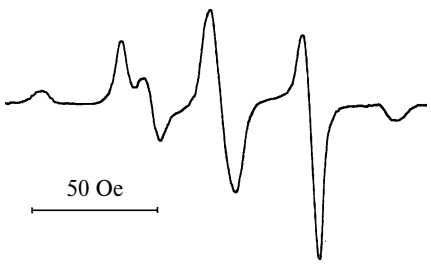
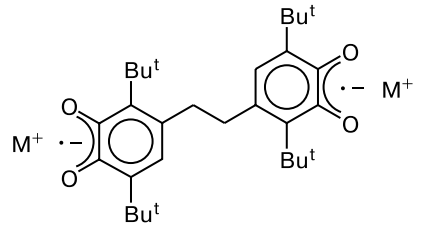
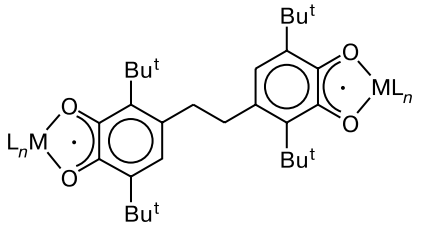


Fig. 3. Anisotropic ESR spectrum of biradical **13** in the 2-methyltetrahydrofuran matrix ($T = 130$ K).



12, 13



14, 15

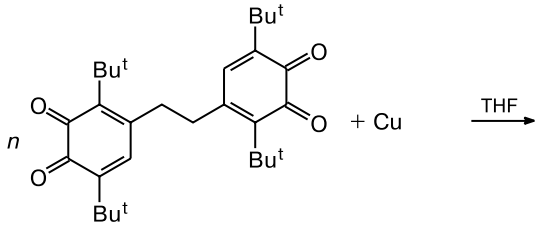
M = Li (**12**), Na (**13**); ML_n = Tl (**14**), $Cu(PPh_3)_2$ (**15**)

Table 2. Splitting parameters in the zero field $D_{\|}$ and the average distance between the radical centers in the biradical derivatives of di-*o*-quinone **1**

Complex	$D_{\|}$/mT	*r*/Å
12	14.9	7.2
13	14.0	7.4
14	14.5	7.3
15	10.0	8.2

di-*o*-quinone **1** (Scheme 1) and studied its magnetochemical properties.

Scheme 1



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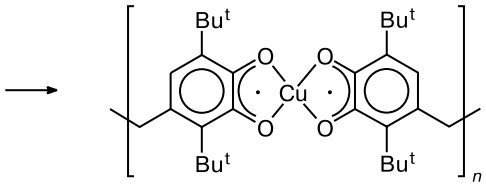
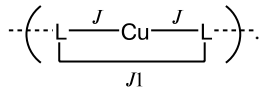


16

The effective magnetic moment μ_{eff} of the polymer (based on the repeated fragment SQ—Cu^{II}—SQ) varies from 1.75β at 2 K to 2.59β at 300 K. The high-temperature μ_{eff} value is close to that for three independent unpaired electrons in the molecule (one electron per Cu^{II} atom (d^9) and each of the two *o*-semiquinone ligands). The low-temperature μ_{eff} value approaches μ_{eff} for one unpaired electron, which indicates the predominantly antiferromagnetic exchange interactions between unpaired electrons of the copper ion and paramagnetic ligands coordinated by this ion. Theoretical analysis of the temperature plot of the magnetic susceptibility of the polymeric complex was performed in the framework of the HDVV model.[17] The scheme and program for calculation of heterospin clusters are described.[18] In particular, for the calculation of this polymeric complex, we chosen a heterospin exchange cluster, being a repeating trimer in which the copper ion is directly coordinated to two SQ ligands



This choice suggested that the exchange interactions *J* and *J*1 are much higher than the interactions between particular trimers in the chain, because the L—L distances in the adjacent trimers are ~7 Å, and the intercluster exchange parameter *J′z* (*z* is the number of the nearest neighbors of the clusters) took into account the exchange interactions between the trimers belonging to particular chains and between different chains. The optimum parameters of the spin-Hamiltonian g_{Cu}, *J*, *J*1, and *J′z* (g_L was accepted equal to 2) were obtained by the optimization of the root-mean-square deviation

$$\sigma = \sum_{i=1}^{n}\left[\mu_{eff}^{exp}(T_i) - \mu_{eff}^{calc}(T_i)\right]^2.$$

As a result, the following parameters were found: g_{Cu} = 2.12±0.01, *J* = −(61±1)K (−42 cm^{-1}), *J*1 = −(150±2)K (−104 cm^{-1}), *J′z* = −(0.5±0.11)K (−0.35 cm^{-1}), σ = 0.00153. The calculated curve $\mu_{eff}(T)$ corresponding to these parameters (curve *1*) is presented in Fig. 4. Antiferromagnetic exchange is observed between the *o*-semiquinone ligands (*J*1 < 0). Monomeric bis(3,6-di-*tert*-butyl-*o*-benzosemiquinolate)copper(II) (**17**) exhibited somewhat different pattern.[19] The signs of semiquinone ligand—copper(II) exchange interaction in the polymer and monomer are different. Ferromagnetic metal—ligand exchange is observed[19] in square-planar complex **17**, while in compound **16** this exchange interaction is antiferromagnetic. We attempted to approximate the experimental data for compound **16** when *J* are positive and *J*1 are negative (see Fig. 4, curve *2*). As a result, the optimum parameters corresponding to a shallower minimum

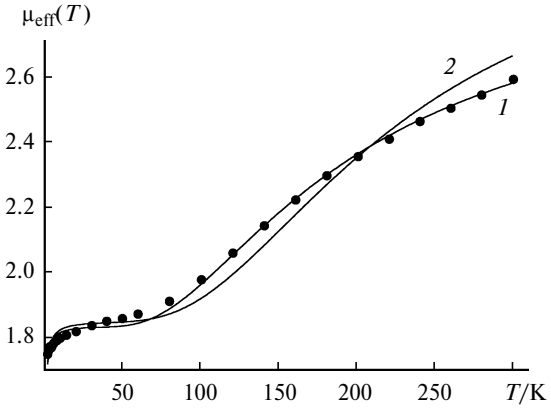


Fig. 4. Experimental (points) and theoretical (curves *1* and *2*) $\mu_{eff}(T)$ plots for coordination polymer **16**.

(higher σ) were obtained: g = 2.14±0.01, J = (204±10)K (142 cm^{-1}), $J1$ = −(328±8)K (−228 cm^{-1}), $J'z$ = −(0.65±0.15)K (−0.45 cm^{-1}), σ = 0.00781. They are close to the values obtained[19] for complex **17**.

As shown previously,[20,21] the geometry of a complex has a critical effect on the sign of the exchange integral in the *o*-semiquinone derivatives of copper(II). For the square-planar structure of the coordination mode, the magnetic π_{SQ}*- and $d_{x^2-y^2}$-orbitals are orthogonal, which produces a strong ferromagnetic exchange. A slight deviation from planarity increases sharply the antiferromagnetic contribution to the metal—ligand exchange interaction, because the direct overlap of the π_{SQ}*- and $d_{x^2-y^2}$-orbitals becomes possible. Most likely, in polymer **16** the coordination environment of the copper atom undergoes some distortion of the square-planar coordination, which changes the sign of the exchange integral J compared to that of its monomeric analog.

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