ESR study of radical anions and *o*-semiquinone metal complexes — 5,5′-di-*tert*-butyl-2,2′-dimethylbiphenyl-3,4,3′,4′-diquinone derivatives

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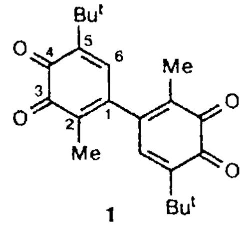
The influence of the nature of the metal (metallofragment) on the spin density distribution in radical anions and *o*-semiquinone metal complexes (derivatives of sterically hindered 5,5′-di-*tert*-butyl-2,2′-dimethylbiphenyl-3,4,3′,4′-diquinone) was studied by ESR spectroscopy. Despite the difference in the characters of the spin density distribution between the radical anion derivatives (M = Li, Na, K, and $CoCp_2$) and *o*-semiquinone complexes (ML_n = Tl, $SnPh_3$, $TlMe_2$, $Cu(PPh_3)_2$, $Cu(CNR)_2$, and $Mn(CO)_4$), in all cases significant delocalization of the spin density of an unpaired electron into the *o*-quinone ring is observed.

Key words: di-*o*-quinone, radical anions, *o*-semiquinone metal complexes; ESR spectroscopy; spin density distribution.

Paramagnetic metallocomplexes, the derivatives of di-*o*-quinones, are a new object of study in the chemistry of *o*-semiquinone metal complexes. Practically all known published data[1—4] on *o*-semiquinone complexes concern mono-*o*-quinone derivatives. It was of interest to study di-*o*-quinone derivatives, which can form bi- and polynuclear complexes due to their bifunctional nature. Di-*o*-semiquinones as bridging ligands provide chemical bonds and even an electron (magnetic) exchange between metallocenters, due to which these complexes can be of interest for molecular electronics[5,6] and designing molecular ferromagnets.[7] In addition, mono- and binuclear metallocomplexes based on di-*o*-quinones are convenient objects for studying intramolecular electronic and magnetic exchange pair metal—ligand and metal—metal interactions.

It is impossible to perform target synthesis of bi- and polynuclear complexes involving di-*o*-semiquinones without detailed studies of the structures of radical ligands and factors controlling the spin density distribution in these molecules.

In order to elucidate the influence of the nature of the metal (metallofragment) on the spin density distribution, here we obtained radical anions and *o*-semiquinone complexes, derivatives of sterically hindered 5,5′-di-*tert*-butyl-2,2′-dimethylbiphenyl-3,4,3′,4′-diquinone (**1**),[8] the radical ion lithium (**2**), sodium (**3**), potassium (**4**), and $CoCp_2$ (**5**) salts; and *o*-semiquinone complexes of various metals in different ligand environments (**6—11**). These substances were studied in solution by ESR spectroscopy.



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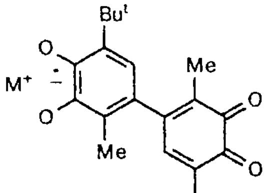
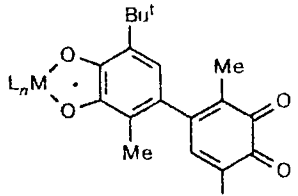


2—5

M = Li (**2**), Na (**3**), K (**4**), $CoCp_2$ (**5**)



6—11

ML_n = Tl (**6**), $SnPh_3$ (**7**), $TlMe_2$ (**8**) $Cu(PPh_3)_2$ (**9**), $Cu(CNR)_2$ (**10**), $Mn(CO)_4$ (**11**)

The ESR spectra of some radical anions and *o*-semiquinone complexes (the derivatives of di-*o*-quinone **1**) are shown in Figs. 1—4. The parameters of the ESR spectra of these and other new compounds studied are presented in Table 1 (the values of isotropic *g*-factors and hyperfine coupling (HFC) constants with other magnetic nuclei in compounds **2—11** are typical of those for similar radicals and complexes and, hence, are not presented in Table 1).

Figures 1—4 and Table 1 show that the spectral parameters reflecting the spin density distribution over the ligand in paramagnetic derivatives, which are formed by the reduction of di-*o*-quinone **1**, depend on the structure of the cation and the character of its bonding

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 904—907, May, 1998.

1066-5285/98/4705-0875 \$20.00

Table 1. Parameters of ESR spectra of radical anions and *o*-semiquinone metal complexes, derivatives of di-*o*-quinone **1**, in solution (290 K)

Complex	M or ML_n	Solvent	a_i(H(6))	a_i(H(6′))	$a_i(CH_3)$	$a_i(CH_3)$
			mT			
2	K	THF	0.260	0.02	0.110	0.130
3	Li	THF	0.265	0.02	0.085	0.085
4	Na	THF	0.260	0.02	0.097	0.113
5	$Co(C_5H_5)_2$	THF	0.260	—	0.095	0.095
6	Tl	THF	0.280	—	0.045	0.045
7	Ph_3Sn	Et_2O[a]	0.245	—	0.070	0.070
7	Ph_3Sn	Et_2O[b]	0.275	—	0.035, 0.070	
8	Me_2Tl	Et_2O	0.270	—	0.070	0.070
9	$(Ph_3P)_2Cu$	Toluene	0.270	—	0.070	0.070
10	$(RNC)_2Cu$	Toluene	0.300	—	0.065	
11	$(OC)_4Mn$	Toluene	0.290	—	0.060	

[a] At 160 K. [b] At 330 K.

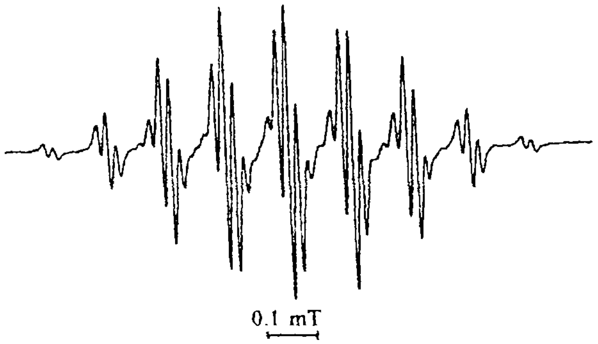


Fig. 1. ESR spectrum of radical anion **4** (M = K; THF, 290 K).

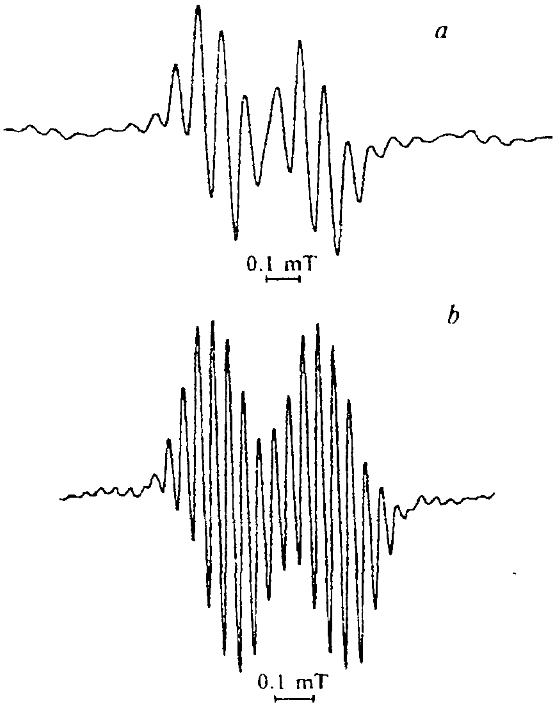


Fig. 2. ESR spectra of *o*-semiquinone complex **7** (ML_n = $SnPh_3$; Et_2O) at 160 K (*a*) and 330 K (*b*).

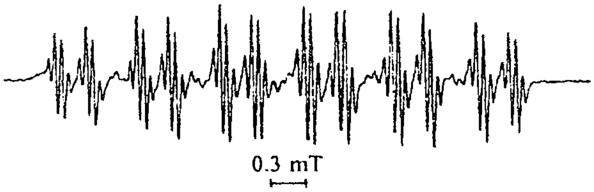


Fig. 3. ESR spectrum of *o*-semiquinone complex **11** (ML_n = $M(CO)_4$; toluene, 290 K).

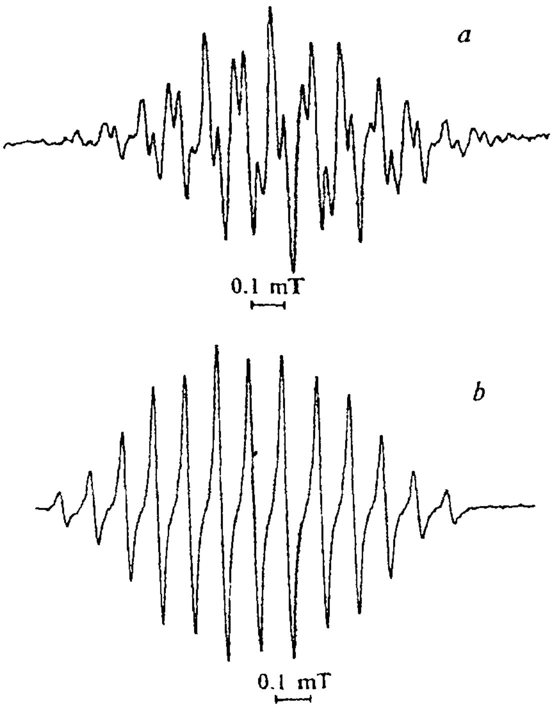


Fig. 4. ESR spectra of phenoxyl radicals **12** (*a*) and **13** (*b*) (toluene, 290 K).

with the radical anion. The ESR spectra of radical ion salts **2**—**5** (see Fig. 1) exhibit HFC of an unpaired electron with the H(6) proton of the semiquinone ring, the protons of two methyl groups in positions 2 and 2′, and for alkali metal salts, with the H(6′) proton of the quinone ring as well. The HFC constant a_i(H(6)) ranges from 0.260 to 0.265 mT for different metals, which is somewhat lower than the values of a_i(H) constants (≥0.3 mT) observed in the ESR spectra of normal *o*-semiquinones. By contrast, the values of the HFC constants with hydrogen atoms of both methyl groups are unusually high: in the case of M = K, they reach 0.11 and 0.13 mT. Note for comparison that in the ESR spectrum of potassium 6-*tert*-butyl-3-methyl-*o*-benzosemiquinolate, $a_i(CH_3)$ = 0.067 mT. The parameters of the ESR spectra for these derivatives are almost temperature-independent.

For derivatives whose metallofragment is covalently bound to the *o*-semiquinone ligand ($SnPh_3$ and $TlMe_2$), a temperature dependence of the ESR spectra is observed, which is related to the known effect of metallotropism[9] inherent in similar *o*-semiquinone complexes.

At low temperatures (Et_2O, 160 K), the ESR spectrum of complex **7** represents a doublet (1 : 1, a_i = 0.245 mT) of septets with the distribution of intensities in the multiplet close to binomial (see Fig. 2, *a*). As in other cases, doublet splitting is due to the hyperfine interaction of an unpaired electron with the proton at the C(6) atom, and septet splitting (a_i = 0.070 mT) is a result of the interaction with six protons of two methyl groups at the C(2) and C(2′) atoms. When the temperature increases, the shape of the ESR spectrum changes. The doublet splitting increases monotonically and reaches 0.275 mT at 330 K. In the multiplets additional components also appear and increase monotonically, so that in the high-temperature limit (see Fig. 2, *b*), each multiplet consists of ten components with 1 : 3 : 6 : 10 : 12 intensity distributions corresponding to HFC with two methyl groups (a_i^1 = 0.070 mT, a_i^2 = 0.035 mT). As the temperature increases, the HFC constant with tin isotopes (^{115}Sn and ^{119}Sn) slightly changes, decreasing from 1.065 mT (at 160 K) to 1.035 mT (at 330 K).

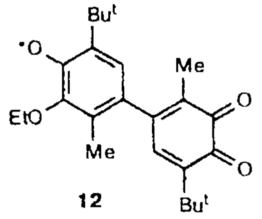
The ESR spectrum of the complex with $TlMe_2$ has similar spectral parameters and exhibits a similar temperature dependence.

In spectral parameters reflecting the spin density distribution over the ligand, the chelate metallocomplex containing the $Cu(PPh_3)_2$ moiety is close to the derivatives containing the $SnPh_3$ and $TlMe_2$ metallofragments. However, in this case, the ESR spectrum is temperature-independent.

The ESR spectra of the metallocomplexes with chelate symmetrical metallofragments of the $Mn(CO)_4$ (see Fig. 3) and $Cu(CNR)_2$ (doublet of quartets) types differ from the spectra of the other complexes. They exhibit HFC with only one proton of the ring and three protons of one methyl group. The doublet splitting (a_i = 0.29 mT) can be safely assigned to HFC with the H(6) proton. It is difficult to assign reliably HFC with the methyl group. Based on available experimental data, it is impossible to make a choice between two possible variants: splitting on protons of the Me group at the C(2) atom in the semiquinone ring or at the C(2′) atom in the quinone ring. The comparison of the ESR spectra of complex **11** and its analog (6-*tert*-butyl-3-methylbenzoquinone-1,2 derivative in which HFC with protons of the methyl group is absent) favors the second variant. However, it should be kept in mind that due to the *o*-quinone substituent in the *o*-semiquinone ring in molecule **11**, its spin density distribution can differ noticeably from that in a similar complex with 6-*tert*-butyl-3-methylbenzosemiquinone.

The observed values of HFC constants are evidence for a substantial delocalization of the spin density in radical anions **2**—**11** over the semiquinone and quinone rings of the ligand. The degree of delocalization depends on two factors: (1) the spin density on the C(1) atom through which the interaction with the quinone ring occurs and (2) the value of the torsion angle (τ) between the plane of the semiquinone and quinone cycles. This angle controls the efficiency of the π—π-interaction between two rings of the di-*o*-quinone ligand.

The role of the first factor can be seen for two isomeric phenoxyls (**12** and **13**), the derivatives of di-*o*-quinone **1**. In phenoxyl **12**, the *o*-quinone ring is in the *para*-position relative to the radical center, due to which a considerable spin density capable of delocalization over the π-system of the *o*-quinone ring is concentrated on the C(1) atom. As a result, the ESR spectrum of this radical contains HFC with both protons of the methyl groups (a_i = 0.12 and 0.21 mT) and the ring protons (a_i = 0.06 and 0.03 mT). In phenoxyl **13**, the *o*-quinone substituent is arranged in the *meta*-position relative to the radical center, due to which the spin density on the C(1) atom is very small, and its delocalization over the *o*-quinone ring is impossible. The HFC with one ring proton (a_i = 0.76 mT) and protons of one methyl group (a_i = 0.42 mT) appears in the ESR spectrum of compound **13**.



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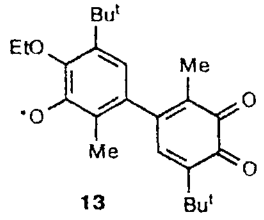

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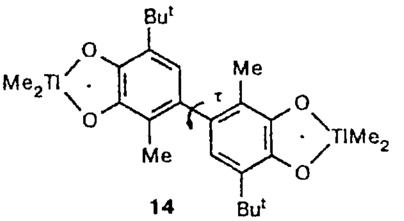
The degree of delocalization of the spin density of an unpaired electron over the second, quinone ring of the paramagnetic ligand should also depend on the value of the τ angle. The spin density delocalization is impossible for the orthogonal arrangement of the rings (τ = 90°), whereas it is maximum when the rings are parallel (τ = 0°). In the latter case, the molecular and electronic structures of the ligand can be close to those of diphenylquinone.

X-ray diffrction data for the *o*-semiquinone derivatives studied in this work have not yet been obtained. It is known, however, that in the starting di-*o*-quinone **1**, the torsion angle $\tau = 82°$.[8] Taking into account that the $\pi-\pi$-interaction is proportional to $\cos^2\tau$, we can conclude that this τ value is unable to provide the spin density localization observed in complexes **2—11**. Probably, the torsion angles in these structures are close to $\tau = 52°$ in the binuclear complex **14**, whose X-ray structural study will be published elsewhere.



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Experimental

ESR spectra were recorded on a Bruker ER 200D-SRC radiospectrometer with a working frequency of 9.5 GHz. An ER 4111 VT series temperature-control block was used for thermostatting samples.

Di-*o*-quinone **1** was synthesized by oxidative coupling of the corresponding mono-*o*-quinone.[8] Solvents (Et_2O, THF, and toluene) were purified according to standard procedures.

The samples for ESR studies were prepared according to a standard procedure including triple cyclic freeze—pump—thaw using known procedures for synthesis of radical anion salts and *o*-semiquinone complexes.[1—4]

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 95-03-09455 and 96-15-97520) and in part by the International Center, Foundation for Promising Studies in Nizhnii Novgorod (MTsFPIN) (Grant 97-3-01). The spectral studies were performed in the TsKP "Analytical Center of the Institute of Molecular Chemistry, Russian Academy of Sciences" with support from the Russian Foundation for Basic Research (Project No. 96-03-40042).

References

1. C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
2. G. A. Abakumov, *Metalloorganicheskie soedineniya i radikaly* [*Organometallic Compounds and Radicals*], Nauka, Moscow, 1985, 85 (in Russian).
3. G. A. Abakumov and V. K. Cherkasov, *Metalloorg. Khim.*, 1990, **3**, 838 [*Organomet. Chem. USSR*, 1990, **3**, 426 (Engl. Transl.)].
4. C. G. Pierpont and C. W. Lange, *Progr. Inorg. Chem.*, 1994, **41**, 331.
5. *Molecular Electronics*, Ed. G. J. Ashwell, Wiley, Chichester, 1992.
6. M. D. Ward, *Chem. Soc. Rev.*, 1995, 121.
7. O. Kahn, *Molecular Magnetism*, VCH, New York, 1993, Ch. 4.
8. G. A. Abakumov, V. I. Nevodchikov, N. O. Druzhkov, L. N. Zakharov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 804 [*Russ. Chem. Bull.*, 1997, **46**, 771 (Engl. Transl.)].
9. M. I. Kabachnik, N. N. Bubnov, A. I. Prokof'ev, and S. P. Solodovnikov, *Sov. Sci. Rev., Ser. B*, 1981, **XXIV**, 197.

Received January 5, 1998