# Functionalization of sterically hindered *o*-benzoquinones: amino-substituted 3,6-di(*tert*-butyl)-*o*-benzoquinones

***G. A. Abakumov, V. K. Cherkasov,* T. N. Kocherova, N. O. Druzhkov, Yu. A. Kurskii, M. P. Bubnov, G. K. Fukin, and L. G. Abakumova***

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
*49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.*
*Fax: +7 (831 2) 12 7497. E-mail: tanya@iomc.ras.ru*

New sterically hindered functionalized *o*-quinones were synthesized by the 1,4-nucleophilic addition of secondary cyclic amines to 3,6-di(*tert*-butyl)-*o*-benzoquinone. The ability of these *o*-quinones to form *o*-semiquinone complexes with transition and main-group metals was studied by ESR spectroscopy in solution.

**Key words:** *o*-quinones, amines, piperazines, nucleophilic addition, *o*-semiquinone metal complexes, charge transfer band, ESR spectroscopy.

Sterically hindered *o*-benzoquinones have attracted interest due to their wide use as the starting compounds in the synthesis of metal complexes with free-radical ligands.[1—3] The introduction of an additional reactive group into *o*-benzoquinone (the functionalization of *o*-benzoquinone)[4—11] extends the coordination potential of the *o*-semiquinone ligand. The synthesis of high-spin polynuclear compounds[12] and coordination polymers[13,14] containing paramagnetic metal ions along with radical *o*-semiquinone ligands is one of the promising applications of such functionalized *o*-quinones (including di-*o*-quinones). The use of functionalized *o*-quinones for the design of paramagnetic probes and labels, which are introduced into systems by reactions leaving intact the paramagnetic center,[15,16] is another remaining undeveloped field of application of these compounds.

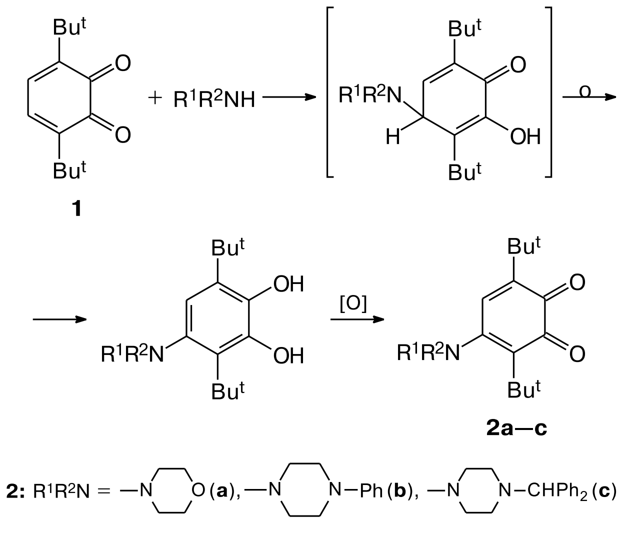
Amines belong to one of the largest classes of ligands used in coordination and organometallic chemistry.[17] In addition, amines can form adducts with simple acids as well as with Lewis acids. *o*-Quinones functionalized by amino groups are of obvious interest as the starting compounds for the synthesis of metal complexes with free-radical ligands.

Earlier,[18] we have reported that the reactions of 3,6-di(*tert*-butyl)-*o*-benzoquinone (**1**) with primary aromatic amines afford the corresponding 2-hydroxy-*p*-quinone imines. *p*-Quinone imine, which is produced in the reactions of primary aliphatic amines, exists in solution in equilibrium with tautomeric 4-amino-*o*-quinone. The reaction with secondary aliphatic amine (piperidine), whose addition product contains no protons capable of migration, yielded new substituted *o*-quinone.

The aim of the present study was to investigate the reactions of **1** with secondary cyclic amines and to synthesize new bifunctional *o*-quinones. The synthesis of morpholine and piperidine derivatives of unsubstituted *o*-benzoquinone is based on the reaction of pyrocatechol with the corresponding amines in the presence of copper(II) salts. However, 4,5-diamino-substituted *o*-quinones thus prepared exist as zwitterionic structures and do not have properties characteristic of *o*-quinones (one-electron reduction and the formation of *o*-semiquinone complexes).[19]

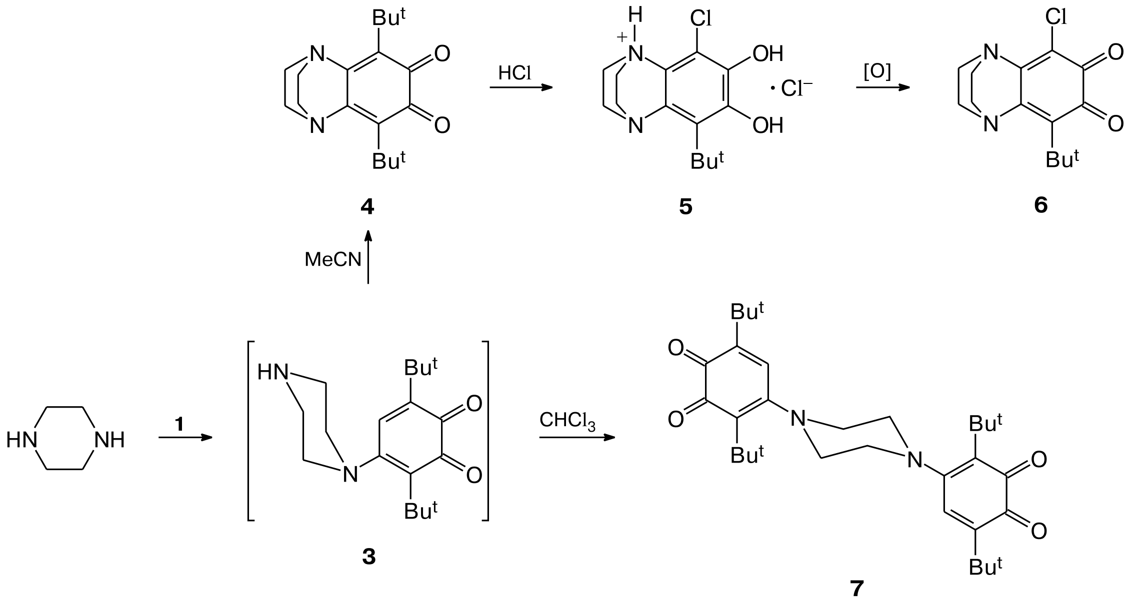
The reactions of quinone **1** with a series of amines (morpholine, 1-phenylpiperazine, and 1-diphenylmethylpiperazine) in acetonitrile at room temperature followed by oxidation of the reaction mixture with an alkali solution of potassium ferricyanide afford 4-amino-3,6-di(*tert*-butyl)-*o*-benzoquinones **2a—c** in high yields (Scheme 1).

**Scheme 1**



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1786—1793, September, 2007.

**Scheme 2**



Unsubstituted piperazine contains two reaction centers due to which its reaction with quinone **1** does not stops at 4-piperazinyl-substituted *o*-quinone; instead, it affords, depending on the reaction conditions, two different products (Scheme 2). The reaction of equimolar amounts of the reagents in acetonitrile involves the second, intramolecular nucleophilic addition, reaction giving rise finally to tricyclic 5,8-di(*tert*-butyl)-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione (**4**).

In compound **4**, the piperazine rings adopts a rigid boat conformation. Four protons of this ring are constantly in axial positions, and the other four protons are in equatorial positions. In the $^1$H NMR spectrum, two $NCH_2CH_2N$ fragments are manifested as an AA′BB′ system. The $H_A$ and $H_B$ ($H_{A'}$ and $H_{B'}$) protons are geminal, the $H_A$ and $H_{A'}$ ($H_B$ and $H_{B'}$) protons are in a synperiplanar conformation, and the $H_A$ and $H_{B'}$ ($H_{A'}$ and $H_B$) protons are in an anticlinal conformation. The chemical shifts are $\delta_A$ = 2.89 and $\delta_B$ = 3.04. The spin-spin coupling constants are $^3J_{AA'} = J_{BB'} = 9.6$ Hz, $^2J_{A'B'} = J_{AB} = -12.9$ Hz, and $^3J_{AB'} = J_{A'B} = 6.5$ Hz.

In the reaction of piperazine with an excess of quinone **1** in chloroform, the intramolecular cyclization slows down (the yield of tricyclic product **4** is at most 15—20%), and the competitive reaction of the free NH group of the piperazine fragment with the second molecule **1** becomes predominant, resulting in the formation of bis-*o*-quinone **7** in 50—55% yield based on consumed piperazine.

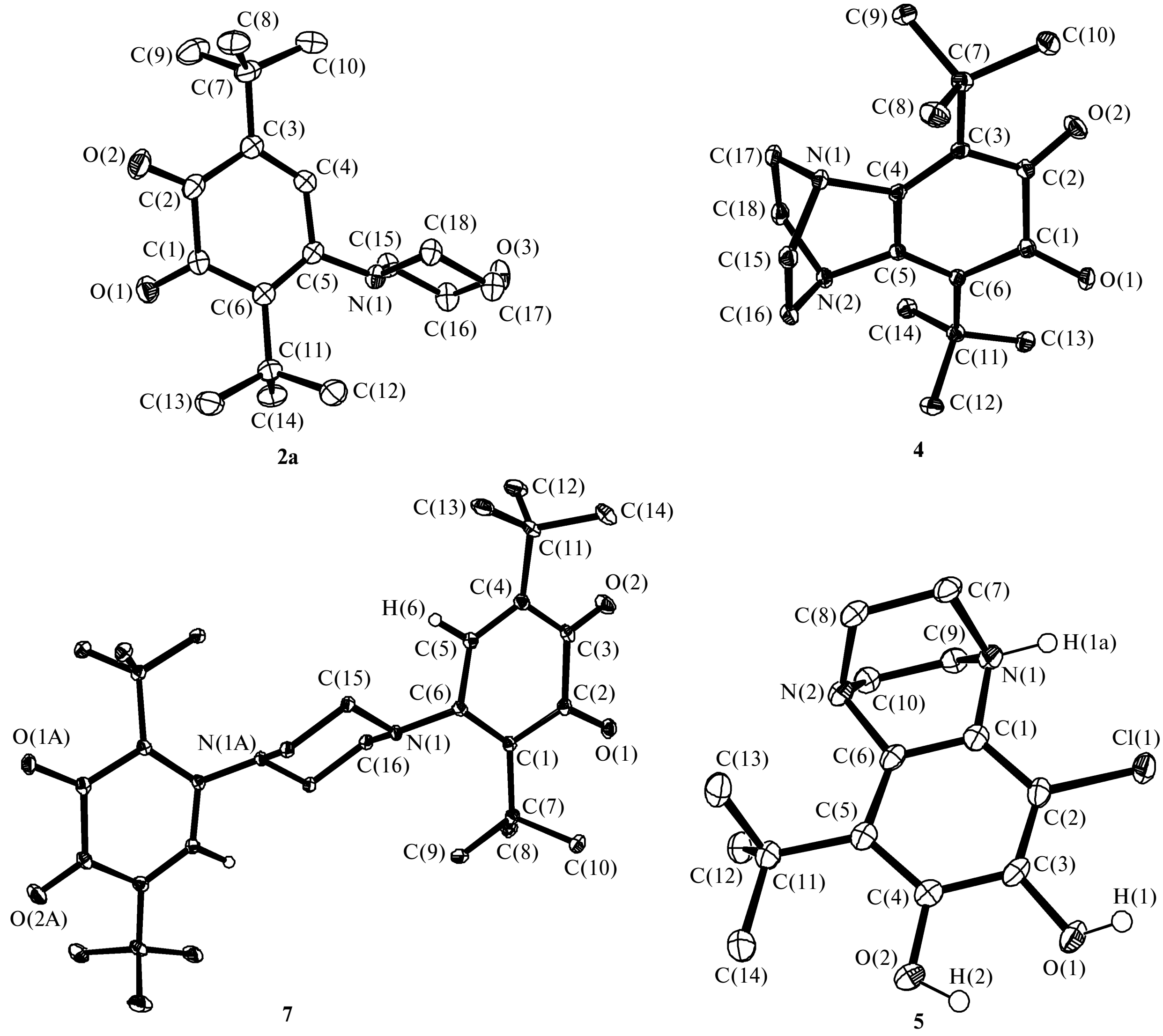
The treatment of quinone **4** with concentrated hydrochloric acid involves the reduction[20] giving rise to a salt accompanied by the replacement of one *tert*-butyl group by the chlorine atom. The molecular structure of pyrocatechol salt **5** was confirmed by X-ray diffraction (Fig. 1). The subsequent oxidation of compound **5** affords 5-*tert*-butyl-8-chloro-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione (**6**).

The structures of all new *o*-quinones were confirmed by elemental analysis, IR spectroscopy, and $^1$H and $^{13}$C NMR spectroscopy. The molecular structures of compounds **2a**, **4**, **5**, and **7** were established by X-ray diffraction.

The structures of *o*-benzoquinones **2a**, **4**, and **7** are characterized by the noncoplanarity of the cyclohexadienone ring. The OCCO torsion angles are 26.4, 43.7, and 12.8° for *o*-benzoquinones **2a**, **4**, and **7**, respectively. As opposed to compounds **2a**, **4**, and **7**, the corresponding angle in **5** is 1.4°. Therefore, the introduction of a bulky substituent at position 4 of the ring adjacent to the *tert*-butyl group in compounds **2a**, **4**, and **7** leads to a substantial distortion of the geometry of the OCCO fragment. In the absence of bulky substituents in the adjacent positions of quinone, the OCCO torsion angles are 2.40—6.54°.[21—24] Apparently, the minimization of nonbonded interactions between the substituent at position 4 of the ring and the *tert*-butyl group is responsible for a deviation of the oxygen atoms from the plane of the molecule.

The C—C and C—O bond lengths in the quinone fragment are typical of *o*-benzoquinones[21—25] (Table 1).

The electronic absorption spectrum of the starting *o*-quinone **1** (Table 2) in dichloromethane at 290 K shows two absorption bands[26] with maxima at 415 nm ($\varepsilon$ = 2500 L mol$^{-1}$ cm$^{-1}$) and 584 nm

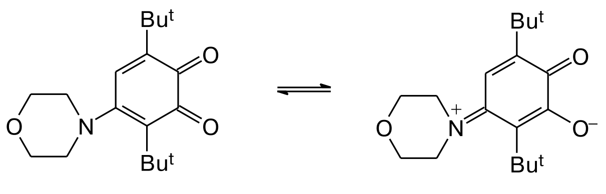


**2a** **4** **7** **5**

**Fig. 1.** Molecular structures of compounds **2a**, **4**, **5**, and **7**.

($\varepsilon = 100$ L mol$^{-1}$ cm$^{-1}$). Under analogous conditions, the electronic absorption spectra of 4-*N*-substituted *o*-quinones **2a—c** and **7** contain, along with absorption bands characteristic of *o*-quinones, an electron transfer band with a maximum at 500 nm corresponding to the intramolecular charge transfer between the electron-donating (piperidine) fragment and the electron-withdrawing (quinone) fragment of the molecule (Fig. 2, Scheme 3).

**Scheme 3**



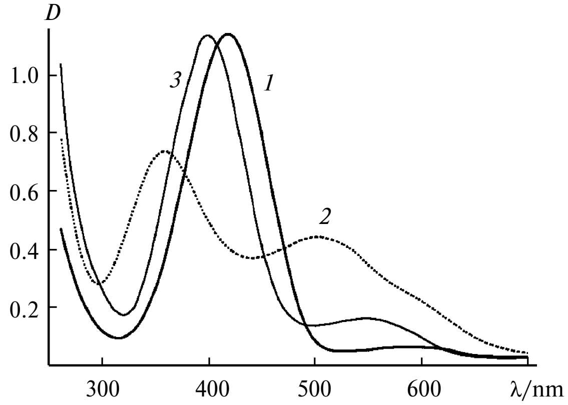


**Fig. 2.** Electronic absorption spectra of compounds **1** (*1*), **2a** (*2*), and **4** (*3*) (dichloromethane).

To the contrary, the electronic absorption spectra of 4,5-*N*,*N*-disubstituted *o*-quinones **4** and **6**, like that

**Table 1.** Selected bond lengths ($d$), bond angles ($\omega$), and torsion angles ($\theta$) in molecules **2a**, **4**, **5**, and **7**

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| Molecule **2a** | | Molecule **4** | |
| Bond | $d$/Å | Bond | $d$/Å |
| O(1)—C(1) | 1.217(2) | O(1)—C(1) | 1.213(2) |
| O(2)—C(2) | 1.215(2) | N(1)—C(4) | 1.438(2) |
| N(1)—C(5) | 1.437(2) | C(1)—C(6) | 1.477(2) |
| C(1)—C(6) | 1.479(2) | C(1)—C(2) | 1.550(2) |
| C(1)—C(2) | 1.547(2) | N(2)—C(5) | 1.444(2) |
| C(2)—C(3) | 1.472(2) | O(2)—C(2) | 1.212(2) |
| C(3)—C(4) | 1.341(2) | C(2)—C(3) | 1.477(2) |
| C(4)—C(5) | 1.474(2) | C(3)—C(4) | 1.351(2) |
| C(5)—C(6) | 1.357(2) | C(4)—C(5) | 1.495(2) |
| | | C(5)—C(6) | 1.353(2) |
| Angle | $\omega$/deg | Angle | $\omega$/deg |
| O(1)—C(1)—C(2) | 116.38(14) | O(1)—C(1)—C(2) | 116.54(12) |
| O(2)—C(2)—C(1) | 117.22(14) | O(2)—C(2)—C(1) | 116.51(12) |
| C(6)—C(5)—N(1) | 120.93(13) | C(3)—C(4)—N(1) | 122.68(12) |
| N(1)—C(5)—C(4) | 116.26(13) | N(1)—C(4)—C(5) | 112.20(11) |
| | | C(6)—C(5)—N(2) | 122.96(12) |
| | | N(2)—C(5)—C(4) | 111.93(11) |
| Angle | $\theta$/deg | Angle | $\theta$/deg |
| O(1)—C(1)—C(2)—O(2) | 26.4 | O(1)—C(1)—C(2)—O(2) | 43.7 |
| Molecule **5** | | Molecule **7** | |
| Bond | $d$/Å | Bond | $d$/Å |
| Cl(1)—C(2) | 1.735(1) | O(1)—C(3) | 1.221(2) |
| N(1)—C(1) | 1.462(2) | O(2)—C(4) | 1.218(2) |
| N(2)—C(6) | 1.450 (2) | N(1)—C(1) | 1.399(2) |
| O(1)—C(3) | 1.357(2) | C(1)—C(2) | 1.376(2) |
| O(2)—C(4) | 1.361(2) | C(1)—C(6) | 1.481(2) |
| C(1)—C(6) | 1.377(2) | C(2)—C(3) | 1.464(2) |
| C(1)—C(2) | 1.381(2) | C(3)—C(4) | 1.557(2) |
| C(2)—C(3) | 1.385(2) | C(4)—C(5) | 1.469(2) |
| C(3)—C(4) | 1.405(2) | C(5)—C(6) | 1.340(2) |
| C(4)—C(5) | 1.408(2) | | |
| Angle | $\omega$/deg | Angle | $\omega$/deg |
| O(1)—C(3)—C(4) | 115.60(12) | C(2)—C(1)—N(1) | 122.81(12) |
| O(2)—C(4)—C(3) | 116.17(13) | N(1)—C(1)—C(6) | 115.85(11) |
| C(2)—C(1)—N(1) | 124.20(12) | O(1)—C(3)—C(4) | 115.30(12) |
| C(5)—C(6)—N(2) | 124.71(12) | O(2)—C(4)—C(3) | 117.13(13) |
| Angle | $\theta$/deg | Angle | $\theta$/deg |
| O(1)—C(3)—C(4)—O(2) | 1.4 | O(1)—C(3)—C(4)—O(2) | 12.8 |

of **1**, show only two absorption bands with maxima at 395 and 545 nm ($\varepsilon$ = 2100 L mol$^{-1}$ cm$^{-1}$ and $\varepsilon$ = 230 L mol$^{-1}$ cm$^{-1}$) for **4** and at 420 and 560 nm ($\varepsilon$ = 2300 L mol$^{-1}$ cm$^{-1}$ and $\varepsilon$ = 260 L mol$^{-1}$ cm$^{-1}$) for **6**. The charge transfer band in the spectra of these compounds is absent, because the rigid molecular structure strictly determines the orientation of the lone electron pair of the nitrogen atom, thus excluding the possibility of its conjugation with the quinone ring.

All new *o*-quinones can undergo one-electron reduction to form radical anions and, consequently, they are potential ligands for free-radical metal complexes. The ESR spectra of potassium *o*-semiquinolates **2a—c** and **7** in THF are doublets due to the hyperfine coupling between the unpaired electron and the hydrogen atom nucleus at position 5 of the semiquinone ring (Table 3). The hyperfine coupling with other magnetic nuclei is not observed in the ESR spectra; however, it makes a contribution to the widths of individual components of the spectra. The ESR spectrum of potassium *o*-semiquinolate **4** ($g_i$ = 2.0048) has a more complex structure (Fig. 3) and shows the hyperfine coupling of the unpaired electron with two nitrogen atom nuclei ($^{14}$N, $I = 1$, $a_i$(2N) = 0.040 mT) and four equivalent protons of the $\alpha$-methylene groups of the piperazine fragment ($a_i$(4H$_\alpha$) = 0.115 mT).

**Table 2.** Spectroscopic characteristics of *o*-quinones, the positions of absorption maxima (λ/nm), and the corresponding extinction coefficients (ε/L $mol^{-1}$ $cm^{-1}$)

| *o*-Quinone | $\lambda\pi\pi^*$ (ε) | | $\lambda_q$ (ε)* | | λ nπ* (ε) | |
|---|---|---|---|---|---|---|
| | Hexane | $CH_2Cl_2$ | Hexane | $CH_2Cl_2$ | Hexane | $CH_2Cl_2$ |
| **1** | 397<br>(3000) | 415<br>(2500) | — | — | 595<br>(80) | 584<br>(100) |
| **2a** | 366<br>(2200) | 355<br>(2700) | 470<br>(780) | 500<br>(1550) | 597<br>(140) | 590<br>(600) |
| **2b** | 365<br>(2150) | 347<br>(2800) | 495<br>(650) | 507<br>(1800) | 600<br>(140) | 602<br>(850) |
| **2c** | 358<br>(2500) | 349<br>(3600) | 468<br>(1200) | 515<br>(2400) | 603<br>(190) | 596<br>(1300) |
| **4** | 377<br>(2800) | 395<br>(2100) | — | — | 551<br>(180) | 545<br>(230) |
| **6** | 405<br>(3200) | 420<br>(2300) | — | — | 579<br>(160) | 560<br>(260) |
| **7** | ** | 354<br>(5700) | ** | 502<br>(3700) | ** | 598<br>(1300) |

* $\lambda_q$ is the charge transfer band.

** Insoluble.

**Table 3.** ESR parameters of radical anions **2a—c** and **7** (THF, 290 K)

| Radical anion | $g_i$ | $a_i$ (1H) | Linewidth |
|---|---|---|---|
| | | mT | |
| $\mathbf{2a}^{-\bullet}$ | 2.0047±0.0002 | 0.340 | 0.050 |
| $\mathbf{2b}^{-\bullet}$ | 2.0050±0.0002 | 0.340 | 0.065 |
| $\mathbf{2c}^{-\bullet}$ | 2.0050±0.0002 | 0.340 | 0.060 |
| $\mathbf{7}^{-\bullet}$ | 2.0052±0.0002 | 0.334 | 0.075 |

The diquinone nature of compound **7** is manifested in the course of its chemical reduction with mercury in the presence of lithium chloride in THF.[27] The ESR spectral pattern in a frozen solvent matrix (130 K) is typical of biradical species with an axial symmetry of the D tensor. The zero-field splitting parameter *D* is 3.5 mT. This *D* parameter corresponds to the distance between the paramagnetic centers $r = 11.6$ Å,[28] which agrees well with the X-ray diffraction data.

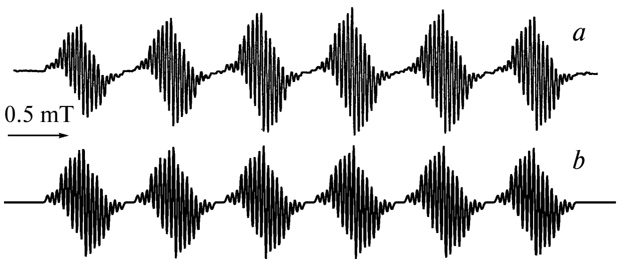
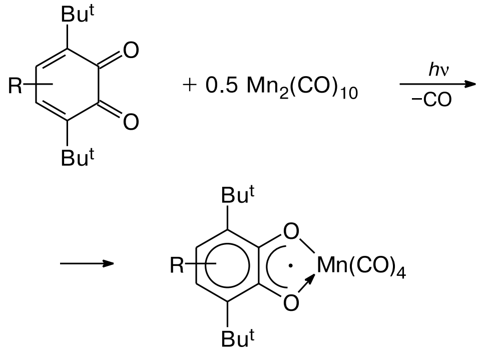


**Fig. 3.** Isotropic ESR spectrum of manganese tetracarbonyl *o*-semiquinolate **4** in toluene at 290 K: *a*, experimental; *b*, simulated.

The formation of paramagnetic complexes was detected in the reactions of *o*-quinones with $Mn_2(CO)_{10}$ performed under visible light irradiation in toluene (Scheme 4). The ESR spectra of chelate *o*-semiquinone manganese tetracarbonyl complexes **2a—c** show the hyperfine coupling of the unpaired electron with magnetic isotopes of one manganese atom ($^{55}$Mn, $I = 5/2$, 100% (see Ref. 29)), the amino nitrogen atom, the proton at position 5 of the quinone ring, and two α-methylene protons of the substituent (Table 4).

**Scheme 4**



Due to the replacement of the *tert*-butyl group in *o*-quinone **6** by the chlorine atom, the molecule becomes asymmetric, and the corresponding ESR spectra have a more complex hyperfine structure compared to that of its symmetric analog **4**. The isotropic ESR spectrum of potassium *o*-semiquinolate **6** is presented in Fig. 4. Its hyperfine coupling constant is determined by interactions of the unpaired electron with two nonequivalent nitrogen atoms ($a_i(^{14}N) = 0.040$ mT and $a_i(^{14}N) = 0.035$ mT) and two pairs of equivalent protons in the α position of the piperazine substituent ($a_i(2^1H) = 0.130$ mT and $a_i(2^1H) = 0.102$ mT). The ESR spectrum of the paramagnetic complex prepared by the reaction of *o*-quinone **6** with $Mn_2(CO)_{10}$ has six groups of lines as a consequence of the hyperfine coupling of the unpaired electron with the magnetic isotope $^{55}$Mn of one manganese atom

**Table 4.** ESR parameters of the chelate complexes formed by the reactions of *o*-quinones **2a—c** and **4** with manganese pentacarbonyl (toluene, 290 K)

| Starting *o*-quinone | $g_i$ | $a_i$ (Mn) | $a_i$ ($H_5$) | $a_i$ (N) | $a_i$ (2Hα) |
|---|---|---|---|---|---|
| | | mT | | | |
| **2a** | 2.0034±0.0002 | 0.690 | 0.340 | 0.050 | 0.040 |
| **2b** | 2.0036±0.0002 | 0.680 | 0.340 | 0.040 | 0.040 |
| **2c** | 2.0031±0.0002 | 0.680 | 0.340 | 0.050 | 0.060 |
| **4** | 2.0037±0.0002 | 0.712 | — | 0.035<br>(2N) | 0.105<br>($4H_\alpha$) |

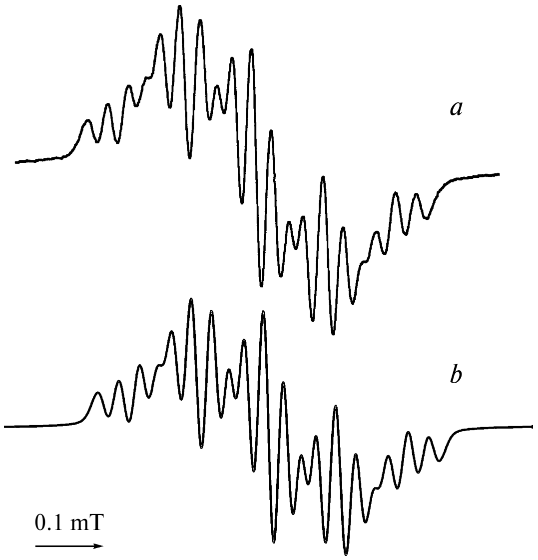


**Fig. 4.** Isotropic ESR spectrum of potassium *o*-semiquinolate **6** (THF, 290 K, $g_i = 2.0047$): *a*, experimental; *b*, simulated.

($a_i(^{55}Mn) = 0.768$ mT), each group of lines having a quintet structure analogous to that observed in the poorly resolved spectrum with potassium. The constants $a_i(^{14}N)$ and $a_i(^1H)$ were not precisely determined because of large linewidths.

## Experimental

The NMR spectra were recorded on a Bruker Avance DPX-200 spectrometer (200 MHz for $^1H$ and 50 MHz for $^{13}C$) with $Me_4Si$ as the internal standard. The ESR spectra were measured on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator operating at 9.5 GHz. The spectra were simulated with the use of the WinESR SimFonia v1.25 Bruker software. The *g* factors were measured using diphenylpicrylhydrazyl as the standard. The electronic absorption spectra were recorded on a Perkin—Elmer Lambda-25 spectrophotometer. The IR spectra were measured on a Specord M-80 spectrometer. X-ray diffraction data sets were collected on an automated Smart APEX diffractometer (graphite monochromator, MoKα radiation, ω—φ-scanning technique, the exposure time per frame was 10 s) at 100 K for all compounds. The X-ray data collection and refinement statistics are given in Table 5. All structures were solved by direct methods and refined by the full-matrix least-squares method based on $F^2_{hkl}$ with anisotropic displacement parameters for all nonhydrogen atoms.

**Table 5.** X-ray data collection and refinement statistics for compounds **2a**, **4**, **5**, and **7**

| Compound | **2a** | **4** | **5** | **7** |
|---|---|---|---|---|
| Molecular formula | $C_{18}H_{27}NO_3$ | $C_{18}H_{26}N_2O_2$ | $C_{17}H_{28}Cl_2N_2O_4$ | $C_{32}H_{46}N_2O_4$ |
| Molecular weight | 305.41 | 302.41 | 395.31 | 522.71 |
| Crystal dimension/mm | 0.22×0.19×0.10 | 0.34×0.16×0.16 | 0.50×0.10×0.10 | 0.27×0.19×0.12 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | *C*2/*c* | *P*2(1)/*n* | $P\bar{1}$ | *P*2(1)/*c* |
| *a*/Å | 18.786(1) | 11.478(8) | 7.359(6) | 10.121(6) |
| *b*/Å | 18.819(1) | 8.7182(6) | 8.748(8) | 10.940(6) |
| *c*/Å | 20.349(1) | 16.823(1) | 15.769(14) | 13.491(8) |
| α/deg | 90 | 90 | 96.126(2) | 90 |
| β/deg | 94.02(2) | 90.014(2) | 101.849(2) | 103.015(1) |
| γ/deg | 90 | 90 | 99.418(2) | 90 |
| $V/Å^3$ | 7176.4(9) | 1683.4(2) | 969.79(15) | 1455.30(15) |
| *Z* | 16 | 4 | 2 | 2 |
| $d_{calc}/g\ cm^{-3}$ | 1.131 | 1.193 | 1.354 | 1.192 |
| $\mu/mm^{-1}$ | 0.076 | 0.078 | 0.358 | 0.078 |
| *F*(000) | 2656 | 656 | 420 | 568 |
| *T*/K | 100(2) | 100(2) | 100(2) | 100(2) |
| θ-Scan range/deg | 1.76—26.50 | 2.15—25.99 | 2.39—26.00 | 2.07—26.00 |
| Index ranges | $-23 \le h \le 17$,<br>$-23 \le k \le 23$,<br>$-25 \le l \le 25$ | $-14 \le h \le 14$,<br>$-9 \le k \le 10$,<br>$-17 \le l \le 20$ | $-8 \le h \le 9$,<br>$-10 \le k \le 7$,<br>$-18 \le l \le 19$ | $-12 \le h \le 12$,<br>$-13 \le k \le 13$,<br>$-16 \le l \le 16$ |
| Number of measured reflections | 22010 | 9632 | 5845 | 12371 |
| Number of independent reflections ($R_{int}$) | 7435 (0.0552) | 3309 (0.0319) | 3779 (0.0159) | 2877 (0.0299) |
| Number of variables | 613 | 303 | 338 | 264 |
| $R_1$ ($I \ge 2\sigma(I)$) | 0.0447 | 0.0405 | 0.0409 | 0.0420 |
| $wR_2$ (based on all reflections) | 0.0898 | 0.0943 | 0.0910 | 0.1005 |
| Goodness-of-fit on $F^2$ | 0.951 | 1.025 | 1.063 | 1.042 |
| Residual electron density (max/min) /e $Å^{-3}$ | 0.254/–0.193 | 0.283/–0.164 | 0.376/–0.232 | 0.345/–0.153 |
| CCDC number | 645416 | 645417 | 645418 | 645419 |

The H atoms in all structures were located in difference electron density maps and refined isotropically. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[30]

The solvents were purified and dried according to standard procedures.[31] 3,6-Di(*tert*-butyl)-*o*-benzoquinone was synthesized according to a known procedure.[32] Morpholine (Khimreaktiv), piperazine (Fluka), 1-(diphenylmethyl)piperazine (Fluka), and 1-phenylpiperazine (Acros) are commercially available reagents.

**3,6-Di(*tert*-butyl)-4-(morpholin-4-yl)-1,2-benzoquinone (2a).** 3,6-Di(*tert*-butyl)-*o*-benzoquinone (1 g, 4.5 mmol) and morpholine (0.3 mL, 4.5 mmol) were dissolved in MeCN (50 mL). The reaction mixture was magnetically stirred at ~20 °C for 3 h. Then the mixture was oxidized by adding it to a vigorously stirred solution of potassium ferricyanide (10 g), $Na_2CO_3$ (3 g), and KOH (0.2 g) in water (100 mL). After completion of the reaction, water (300 mL) was added, and the quinone that precipitated was filtered off, washed, and dried. After recrystallization from hexane, cherry-colored crystals were obtained in a yield of 1.14 g (82%), m.p. 135—137 °C. Found (%): C, 71.05; H, 8.74. $C_{18}H_{27}NO_3$. Calculated (%): C, 70.79; H, 8.91. IR (Nujol mulls), $\nu/cm^{-1}$: 1690, 1685, 1670, 1625, 1565, 1490, 1395, 1365, 1320, 1300, 1265, 1225, 1200, 1115, 1065, 1035, 1025, 1000, 920, 910, 805, 610. $^1H$ NMR ($CDCl_3$, 200 MHz), δ: 1.24 and 1.36 (both s, 9 H each, $Bu^t$); 2.96—3.01 (m, 4 H, N—$CH_2$); 3.79—3.84 (m, 4 H, O—$CH_2$); 6.91 (s, 1 H, H(5)). $^{13}C$ NMR ($CDCl_3$, 50 MHz), δ: 29.1 and 30.8 ($C(\underline{C}H_3)_3$); 35.2 and 36.0 ($\underline{C}(CH_3)_3$); 51.3 (CH (N—$CH_2$)); 66.5 (CH (O—$CH_2$)); 132.8 (CH(5)); 140.0, 148.4, and 156.0 (C(3), C(4) and C(6)); 182.4 and 185.2 (C=O).

**4-(4-Phenylpiperazin-1-yl)-3,6-di(*tert*-butyl)-1,2-benzoquinone (2b).** 3,6-Di(*tert*-butyl)-*o*-benzoquinone (1 g, 4.5 mmol) and 1-phenylpiperazine (0.7 mL, 4.5 mmol) were dissolved in MeCN (50 mL). The reaction mixture was magnetically stirred at ~20 °C for 2 h. Then the mixture was oxidized by adding it to a vigorously stirred solution of potassium ferricyanide (10 g), $Na_2CO_3$ (3 g), and KOH (0.2 g) in water (100 mL). After completion of the reaction, water (300 mL) was added, and the quinone that precipitated was filtered off, washed, and recrystallized from petroleum ether. Crystals were obtained in a yield of 1.34 g (78%), m.p. 132—135 °C. Found (%): C, 75.49; H, 8.53. $C_{24}H_{32}N_2O_2$. Calculated (%): C, 75.75; H, 8.48. IR (Nujol mulls), $\nu/cm^{-1}$: 1685, 1650, 1610, 1550, 1510, 1365, 1330, 1285, 1275, 1235, 1200, 1145, 930, 835, 755, 690. $^1H$ NMR ($CDCl_3$, 200 MHz), δ: 1.24 and 1.37 (both s, 9 H each, $Bu^t$); 3.20—3.30 (m, 8 H, N—$CH_2$); 6.89—6.99 (m, 4 H, *m*-, *p*-Ph, H(5)); 7.26—7.35 (m, 2 H, *o*-Ph). $^{13}C$ NMR ($CDCl_3$, 50 MHz), δ: 29.1 and 30.8 ($C(\underline{C}H_3)_3$); 35.1 and 36.0 ($\underline{C}(CH_3)_3$); 49.6 and 51.5 (N—$CH_2$); 116.7 (CH (*o*-Ph)); 120.8 (CH (*p*-Ph)); 129.4 (CH (*m*-Ph)); 132.9 (CH(5)); 138.7, 148.0, and 156.5 (C(3), C(4), C(6)); 151.2 (C—N (Ph)); 182.4 and 184.7 (C=O).

**4-(4-Diphenylmethylpiperazin-1-yl)-3,6-di(*tert*-butyl)-1,2-benzoquinone (2c).** 3,6-Di(*tert*-butyl)-*o*-benzoquinone (1 g, 4.5 mmol) and 1-(diphenylmethyl)piperazine (1.13 g, 4.5 mmol) were dissolved in MeCN (50 mL). The reaction mixture was magnetically stirred at ~20 °C for 5 h. Then the mixture was oxidized by adding it to a vigorously stirred solution of potassium ferricyanide (10 g), $Na_2CO_3$ (3 g), and KOH (0.2 g) in water (100 mL). After 1 h, the product was extracted with diethyl ether, washed to neutral pH, and dried. After recrystallization from hexane, crystals were isolated in a yield of 1.34 g (68%), m.p. 151—152 °C. Found (%): C, 78.89; H, 8.03. $C_{31}H_{38}N_2O_2$. Calculated (%): C, 79.11; H, 8.14. IR (Nujol mulls), $\nu/cm^{-1}$: 1685, 1670, 1620, 1565, 1500, 1470, 1395, 1365, 1290, 1275, 1205, 1135, 1075, 10005, 850, 765, 750, 730, 710, 695. $^1H$ NMR ($CDCl_3$, 200 MHz), δ: 1.23 and 1.30 (both s, 9 H each, $Bu^t$); 2.48—2.52 (m, 4 H, $CH_2$); 3.11—3.16 (m, 4 H, $CH_2$); 4.25 (s, 1 H, CH—$Ph_2$); 6.91 (s, 1 H, H(5)); 7.19—7.33 (m, 6 H, *m*-, *p*-Ph); 7.44 (d, 4 H, *o*-Ph) . $^{13}C$ NMR ($CDCl_3$, 50 MHz), δ: 29.1 and 30.5 ($CH_3$ ($Bu^t$)); 34.9 and 35.7 ($CMe_3$ ($Bu^t$)); 52.1 (N—$CH_2$); 76.3 (Ph—$\underline{C}H_2$—N) 127.2 (CH (*p*-Ph)); 127.8 and 128.7 (CH (*o*-, *m*-Ph)); 133.0 (CH(5)); 135.6 (C—N (Ph)); 142.2, 147.3, and 156.9 (C(3), C(4), C(6)); 182.1 and 183.5 (C=O).

**5,8-Di(*tert*-butyl)-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione (4).** 3,6-Di(*tert*-butyl)-*o*-benzoquinone (1 g, 4.5 mmol) and piperazine (0.4 g, 4.5 mmol) were dissolved in MeCN (50 mL). The reaction mixture was magnetically stirred at ~20 °C for 3 h. Then the mixture was oxidized by adding it to a vigorously stirred solution of potassium ferricyanide (10 g), $Na_2CO_3$ (3 g), and KOH (0.2 g) in water (100 mL). After completion of the reaction, water (300 mL) was added, and the quinone that precipitated was filtered off, washed, and recrystallized from petroleum ether. Dark-red crystals were obtained in a yield of 1.24 g (91%), m.p. 188—190 °C. Found (%): C, 71.63; H, 8.51. $C_{18}H_{26}N_2O_2$. Calculated (%): C, 71.49; H, 8.67. IR (Nujol mulls), $\nu/cm^{-1}$: 1675, 1565, 1490, 1395, 1365, 1350, 1300, 1280, 1230, 1145, 1065, 1000, 980, 865, 845, 825, 775, 650, 545. $^1H$ NMR ($CDCl_3$, 200 MHz), δ: 1.32 (s, 18 H, $Bu^t$); 2.87—3.06 (m, 8 H, N—$CH_2$, $J_{AA'} = J_{BB'} = 9.6$ Hz, $J_{A'B'} = J_{AB} = -12.9$ Hz, $J_{AB'} = J_{A'B} = 6.5$ Hz). $^{13}C$ NMR ($CDCl_3$, 50 MHz), δ: 30.4 ($C(\underline{C}H_3)_3$); 34.8 ($\underline{C}(CH_3)_3$); 47.1 (N—$CH_2$); 142.4 and 158.6 (C (3), C(4), C(5), and C(6)); 190.6 (C=O).

**5-*tert*-Butyl-8-chloro-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione (6).** 5,8-Di(*tert*-butyl)-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione (1 g, 3.3 mmol) was dissolved in concentrated HCl (50 mL). The reaction mixture was magnetically stirred at 80 °C for 1 h. Then the mixture was neutralized with an aqueous alkali solution, extracted with diethyl ether, and dried. After recrystallization from acetone, compound **5** was obtained as white crystals. Compound **5** was oxidized with a solution of potassium ferricyanide (10 g), $Na_2CO_3$ (3 g), and KOH (0.2 g) in water (100 mL), extracted with diethyl ether, and washed to neutral pH. After the removal of diethyl ether, the dry residue was crystallized from petroleum ether. Dark-cherry-colored crystals were obtained in a yield of 0.8 g (86%), m.p. 184—185 °C. Found (%): C, 60.09; H, 5.99; Cl, 12.57. $C_{14}H_{17}ClN_2O_2$. Calculated (%): C, 59.89; H, 6.10; Cl, 12.63. IR (Nujol mulls), $\nu/cm^{-1}$: 1700, 1680, 1655, 1625, 1565, 1365, 1335, 1280, 1250, 1225, 1170, 1150, 1055, 995, 985, 840, 815, 765, 685, 555. $^1H$ NMR ($CDCl_3$, 200 MHz), δ: 1.37 (s, 9 H, $Bu^t$); 2.89—3.26 (m, 8 H, N—$CH_2$). $^{13}C$ NMR ($CDCl_3$, 50 MHz), δ: 30.7 ($C(\underline{C}H_3)_3$); 35.8 ($\underline{C}(CH_3)_3$); 47.2 and 47.3 (N—$CH_2$); 122.9; 142.7; 156.5; 159.7; 177.3, and 183.2 (C=O).

**4,4´-(Piperazine-1,4-diyl)-bis[3,6-di(*tert*-butyl)-1,2-benzoquinone] (7).** 3,6-Di(*tert*-butyl)-*o*-benzoquinone (2.2 g, 10 mmol) and piperazine (0.6 g, 7 mmol) were dissolved in $CHCl_3$ (60 mL). The reaction mixture was magnetically stirred at ~20 °C for 24 h. Then $PbO_2$ (4.5 g) was added, the mixture was kept for 2 h, and unconsumed $PbO_2$ was filtered off. The solvent was removed, and the dry residue was recrystallized from a mixture of $CH_2Cl_2$ and MeCN. Dark-cherry-colored crystals were obtained in a yield of 1.89 g (52%), m.p. 181—182 °C. Found (%): C, 73.65; H, 8.83. $C_{32}H_{46}N_2O_4$. Calculated (%): C, 73.53; H, 8.87. IR (Nujol mulls), $\nu$/cm$^{-1}$: 1685, 1675, 1630, 1535, 1490, 1465, 1405, 1365, 1350, 1285, 1275, 1210, 1140, 1055, 1030, 1015, 940, 925, 885, 840, 725, 685, 655, 600. $^1$H NMR ($CDCl_3$, 200 MHz), $\delta$: 1.25 and 1.38 (both s, 18 H each, Bu$^t$); 3.11 (s, 8 H, $CH_2$); 6.88 (s, 2 H, H(5)). $^{13}$C NMR ($CDCl_3$, 50 MHz), $\delta$: 29.1 and 30.9 ($CH_3$ (Bu$^t$)); 35.2 and 36.1 ($CMe_3$ (Bu$^t$)); 51.0 (N—$CH_2$); 132.6 (CH(5)); 140.0 (br, C—N); 148.5 and 155.8 (C(3), C(6)); 182.3 and 185.1 (C=O).

*o*-Quinone semiquinolates with potassium and magnesium were generated according to known procedures.[33,34]

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 07-03-00711 and 07-03-00819) and the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-4947.2006.3).

## References

1. C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
2. C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331.
3. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219**, 415.
4. M. Ruf, A. M. Lawrence, B. C. Noll, and C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 1992.
5. D. A. Shultz, S. H. Bodnar, K. E. Vostrikova, and J. W. Kampf, *Inorg. Chem.*, 2000, **39**, 6091.
6. D. A. Shultz, J. C. Sloop, and G. Washington, *J. Org. Chem.*, 2006, **71**, 9104.
7. D. A. Shultz, J. C. Sloop, T. Coote, M. Beikmohammadi, J. Kampf, and P. D. Boyle, *Inorg. Chem.*, 2007, **46**, 273.
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. V. A. Kuropatov, V. K. Cherkasov, Yu. A. Kurskii, G. K. Fukin, L. G. Abakumova, and G. A. Abakumov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 683 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 708].
10. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2206 [*Russ. Chem. Bull.*, 1997, **46**, 2093 (Engl. Transl.)].
11. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 357 [*Russ. Chem. Bull.*, 1997, **46**, 337 (Engl. Transl.)].
12. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, V. A. Kuropatov, G. T. Yee, and C. G. Pierpont, *Inorg. Chem.*, 2001, **40**, 2434.
13. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, V. A. Kuropatov, B. C. Noll, and C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 6117.
14. G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, N. O. Druzhkov, and V. N. Ikorskii, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1580 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1627].
15. A. L. Buchachenko and A. M. Vasserman, *Stabil´nye radikaly* [*Stable Radicals*], Khimiya, Moscow, 1973 (in Russian).
16. E. G. Rozantsev, *Svobodnye iminoksil´nye radikaly* [*Free Iminoxyl Radicals*], Khimiya, Moscow, 1970 (in Russian).
17. G. Wilkinson, *Comprehensive Coordination Chemistry*, Pergamon, 1987, v. **2**.
18. G. A. Abakumov, V. K. Cherkasov, T. N. Kocherova, N. O. Druzhkov, Yu. A. Kurskii, and L. G. Abakumova, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1151 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1195].
19. W. Brackman and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, 1955, **74**, 937.
20. I. A. Novikova, V. B. Vol´eva, N. L. Komissarova, I. S. Belostotskaya, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2110 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1997, **46**, 2093 (Engl. Transl.)].
21. A. L. Macdonald and J. Trotter, *J. Chem. Soc., Perkin Trans. 2*, 1973, 476.
22. J. S. Edmonds, M. Nomachi, M. Terasaki, M. Morita, B. W. Skelton, and A. H. White, *Biochem. Biophys. Res. Commun.* 2004, **319**, 556.
23. Y. S. Rosokha, S. V. Lindeman, S. V. Rosokha, and J. K. Kochi, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 4650.
24. Ok-Sang Jung, Yangha Cho, June-Ho Jung, and Youn Soo Sohn, *Bull. Korean Chem. Soc.*, 1994, **15**, 608.
25. H. Weiner and R. G. Finke, *J. Am. Chem. Soc.*, 1999, **121**, 9831.
26. S. A. Chesnokov, V. K. Cherkasov, G. A. Abakumov, O. N. Mamysheva, Yu. V. Chechet, and V. I. Nevodchikov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2258 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2366].
27. G. A. Abakumov, V. A. Muraev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR,* 1974, 1113 [*Docl. Chem.*, 1974, **215** (Engl. Transl.)].
28. J. E. Wertz and J. R. Bolton, *Electron Spin Resonance*, McGraw-Hill Book Company, New York, 1972.
29. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 584.
30. G. M. Sheldrick, *SHELXTL v. 6.12*, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.
31. A. Gordon and R. Ford, *Chemist's Companion*, A Wiley-Interscience Publication, New York—London—Sydney—Toronto, 1972.
32. E. G. Rozantsev and V. D. Sholle, *Organicheskaya khimiya svobodnykh radikalov* [*Organic Chemistry of Free Radicals*], Khimiya, Moscow, 1973, 344 (in Russian).
33. E. Muller, F. Gunter, K. Scheffler, and A. Reiker, *Liebigs Ann. Chem.*, 1965, **688**, 134.
34. B. L. Tumanskii, K. A. Sarbasov, S. P. Solodovnikov, N. N. Bubnov, A. I. Prokof´ev, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR,* 1981, **259**, 611 [*Docl. Chem.*, 1981 (Engl. Transl.)].

*Received May 30, 2007;*
*in revised form September 6, 2007*