Synthesis of magnesium catecholate and *o*-semiquinone complexes by oxidation of the metal with 3,6-di-*tert*-butyl-*o*-benzoquinone

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Oxidation of amalgamated magnesium metal with 3,6-di-*tert*-butyl-*o*-benzoquinone (**1**) in different aprotic organic solvents afforded magnesium catecholate and bis-*o*-semiquinolate complexes. The catecholate derivatives of magnesium $CatMgL_2$ (Cat is the 3,6-di-*tert*-butyl-*o*-benzoquinone dianion, L = THF or Py) were synthesized in high yields in pyridine and tetrahydrofuran, respectively. The reactions in diethyl ether or dimethoxyethane produced hexacoordinated metal bis-*o*-semiquinolates SQ_2MgL_n (SQ is the 3,6-di-*tert*-butyl-*o*-benzoquinone radical anion, L = Et_2O, $n = 2$; L = DME, $n = 1$). The reaction with the use of toluene as the solvent gave a magnesium bis-*o*-semiquinolate complex containing the coordinated unreduced *o*-quinone molecule. The molecular structures of the $[CatMgPy_2]_2$ and $SQ_2Mg \cdot DME$ complexes were established by X-ray diffraction.

Key words: *o*-benzoquinone, magnesium, *o*-semiquinolate, catecholate, ESR, X-ray diffraction.

Investigation of metal complexes with redox-active ligands is one of the promising fields of modern coordination and organometallic chemistry. Among these compounds are those containing various reduced forms of *o*-quinones, *o*-iminoquinones, diimines, and their derivatives. Redox-active ligands can reversibly add one, two, or more electrons without a loss of coordination abilities. Such complexes were synthesized for all, without exception, transition metals.[1] Some of these complexes have unique magnetic and electronic properties.[2—7] Earlier, *o*-semiquinone complexes of main-group metals have been studied *in situ* in solution by ESR spectroscopy.[8] In recent years, *o*-quinone,[9,10] *o*-iminoquinone,[10—12] and diimine[13—16] complexes of main-group metals have attracted increasing interest due to their unusual behavior in reactions with various substrates, such as radicals,[17—21] haloalkenes,[22,23] nitriles,[24] ketones,[25] and oxygen.[9,11]

In the present study, we synthesized and characterized magnesium catecholate and bis-*o*-semiquinolate complexes generated by reduction of 3,6-di-*tert*-butyl-*o*-benzoquinone (**1**) with magnesium metal in aprotic organic solvents.

Results and Discussion

Oxidation of metals by *o*-quinones is widely used for the synthesis of *o*-quinone complexes of main-group metals.[26] The reaction of magnesium with 3,5-di-*tert*-butyl-*o*-benzoquinone was studied by two research groups. The reaction of powdered magnesium with *o*-quinone in refluxing toluene produces the oligomeric bis(3,5-di-*tert*-butyl-*o*-semiquinono)magnesium complex.[27] This complex has an oligomeric structure because of the presence of intermolecular Mg—O—Mg interactions.[27] Compact magnesium reacts with 3,5-di-*tert*-butyl-*o*-benzoquinone at a noticeable rate only in strong donor solvents (DMF, DMSO, or Py).[28,29] The reaction proceeds through the intermediate formation of bis-*o*-semiquinone derivatives. When the metal is in excess, the reaction produces catecholate derivatives of magnesium. However, the resulting complexes were not isolated in the individual state and were identified by UV and ESR spectroscopy. The final reaction products are most rapidly accumulated in pyridine. However, the reaction even in this solvent is completed in 50 h at 70 °C in an eightfold excess of magnesium.[29] Hence, this system is of little use for the preparative synthesis of compounds. Since amalgamation of magnesium facilitates its reactions with carbonyl compounds, we used the amalgamated metal.

The reaction of *o*-quinone **1** with amalgamated magnesium proceeds rather rapidly already at room temperature in different solvents (toluene, diethyl ether, DME, THF, or pyridine). The compositions and structures of the reaction products substantially depend on the nature of the solvent (Scheme 1).

The reaction in a weakly solvating solvent (toluene) is accompanied by a change in the color of the solution to dark-green followed by isolation of a brown finely crystal-

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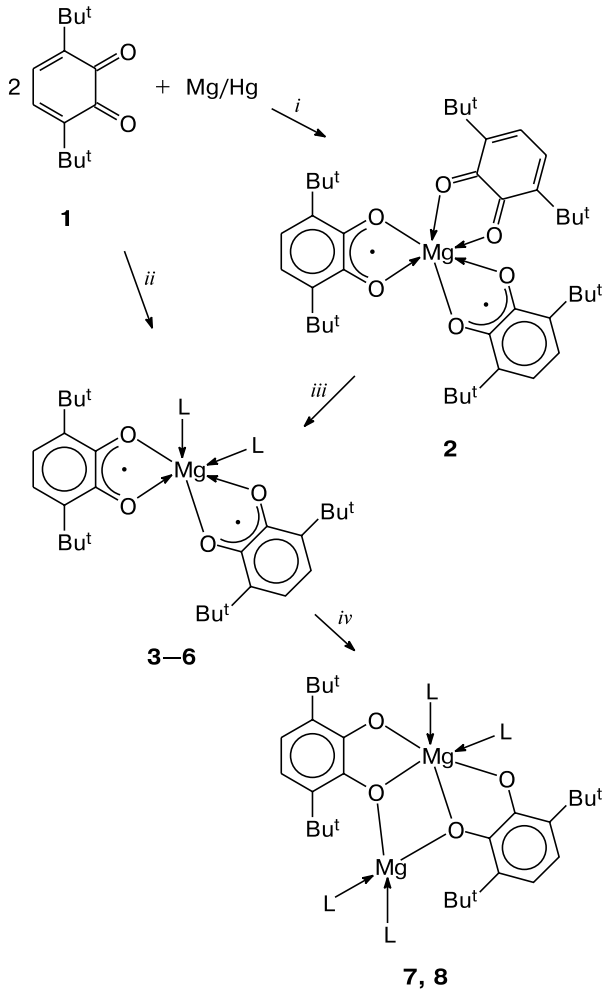
Scheme 1



	3	4	5, 8	6, 7
L	Et_2O	DME	Py	THF
n	2	1	2	2

Reagents: *i.* toluene; *ii.* THF, Et_2O, DME or Py; *iii.* THF, Et_2O, DME, or Py and excess Mg/Hg; *iv.* THF or Py and excess Mg/Hg.

line paramagnetic complex. The composition of this product corresponds to Mg : **1** = 1 : 3. The IR spectrum of a polycrystalline sample shows intense absorption bands in the 1500—1700 cm^{-1} frequency region at 1640 and 1502 cm^{-1}. The former band belongs to stretching vibrations of weakly coordinated *o*-quinone groups[30] (the IR spectrum of the starting *o*-quinone has a band at 1655 cm^{-1}). The latter band is characteristic of radical-anionic derivatives of *o*-quinone **1**.[30] The anisotropic ESR spectrum in the frozen solvent matrix is a superposition of a singlet and signals characteristic of biradical species (Fig. 1, *a*). The spectrum also shows a half-field signal (Δm_s = 2). The zero-field splitting parameters and the distances between the radical centers calculated in the

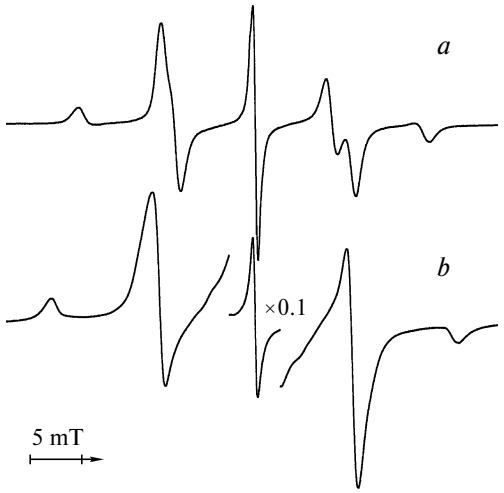


Fig. 1. Anisotropic ESR spectra of complexes **2** (*a*) and **4** (*b*) (2-methyltetrahydrofuran, 130 K).

point-dipole approximation[31] are given in Table 1. The above-described spectroscopic characteristics of the reaction product are indicative of the formation of biradical magnesium complex **2** containing two radical-anion and one unreduced *o*-quinone ligands. The latter ligand can be easily displaced from the coordination sphere of the metal by a coordinating solvent to form complexes **3—6**.

In solvating solvents (ethers or pyridine), the color of the mixture changes to intense blue in the course of the reaction of magnesium with *o*-quinone **1**. The anisotropic spectra of the resulting complexes in the frozen solvent matrix are superpositions of a singlet and signals characteristic of biradical species (Fig. 1, *b*). The spectra also have half-field signals (Δm_s = 2). The ESR spectroscopic parameters of the reaction products are similar to those observed[32] upon generation of bis[3,6-di-(*tert*-butyl)-*o*-benzosemiquinolato]magnesium in the exchange reaction of magnesium chloride and the corresponding radical-anion sodium salt in THF. This is evidence for the formation of bis-*o*-semiquinolate complexes **3—6**.

In diethyl ether and dimethoxyethane, the color of the *o*-semiquinone complexes remains unchanged even upon their prolonged storage over excess magnesium. Com-

Table 1. Zero-field splitting parameters and average distances between the radical centers in biradical complexes **2—6***

Complex	$D_{\parallel}$/mT	*E*/mT	*r*/Å
2	33.6	0.56	5.49
3	41.6	1.03	5.11
4	39.0	~0	5.22
5	33.0	0.55	5.48
6	34.0	0.55	5.47

* 2-Methyltetrahydrofuran was used as the matrix for compounds **2** and **4—6**; toluene, for compound **3**.

plexes **3** and **4** were isolated in the individual state as dark-blue crystalline compounds. The IR spectra of complexes **3** and **4** are virtually identical and show bands (1515, 1502, 1351 cm^{-1}) characteristic of the 3,6-di-*tert*-butyl-*o*-benzosemiquinone ligand.[30]

Unlike the reactions in Et_2O and DME, the reactions in THF and pyridine lead to reduction of magnesium bis-*o*-semiquinolates with excess metal to form catecholate derivatives **7** and **8**, respectively. This process is accompanied by a change in the color of the reaction mixture to colorless or yellow in THF and pyridine, respectively. The resulting complexes are diamagnetic in the crystalline state and in solution and are characterized by well-resolved NMR spectra corresponding to the proposed formulas. The IR spectra show intense absorption bands in the 1200—1300 cm^{-1} region characteristic of C—O single bonds,[9,10,17] which is also evidence for the catecholate structures of the compounds.

The molecular structures of complexes **4** and **8** were established by X-ray diffraction. This is the first example of structurally characterized magnesium complexes with *o*-quinones derivatives. The crystallographic parameters and the X-ray data collection and refinement statistics are given in Table 2. The selected bond lengths and bond angles in molecules **4** and **8** are listed in Tables 3 and 4, respectively.

In molecule **4**, the magnesium atom has a distorted octahedral environment (Fig. 2). The equatorial plane in the octahedron is formed by the O(1), O(3), O(4), and O(5) atoms. The axial positions are occupied by the O(2) and O(6) atoms. The Mg—O(5) and Mg—O(6) distances (2.1067(11) and 2.1242(11) Å, respectively) between the magnesium atom and the oxygen atoms of the coordinated dimethoxyethane ligand are substantially longer than the Mg—O(1), Mg—O(2), Mg—O(3), and Mg—O(4) bonds (2.0257(11)—2.0440(10) Å) formed by the metal atom and the *o*-quinone ligands. The latter bond lengths are larger than those typical of phenolate derivatives of magnesium (1.887(1)—1.914(2) Å)[33] but agree well with the Mg—O distances in magnesium β-diketonate complexes (2.000(2)—2.060(6) Å).[34] The C—O and C—C bond lengths in the diolate ligands confirm its radical-anion character.[35] The dihedral angle between the *o*-benzosemiquinone ligands in complex **4** is 71.5°.

Catecholate complex **8** has a dinuclear structure (Fig. 3). The magnesium atoms in dimer **8** are in different

Table 2. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for complexes **4** and **8**

Parameter	**4**	**8**
Molecular formula	$C_{32}H_{50}MgO_6$	$C_{48}H_{60}Mg_2N_4O_4$
Molecular weight	555.03	805.62
T/K	100(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
a/Å	11.5229(5)	10.611(3)
b/Å	26.3182(11)	10.956(3)
c/Å	11.0791(5)	20.673(5)
α/deg	90	98.664(5)
β/deg	102.2750(10)	96.897(5)
γ/deg	90	100.857(5)
V/Å	3283.1(2)	2306.1(9)
Z	4	2
ρ/g cm^{-3}	1.123	1.160
μ/mm^{-1}	0.092	0.098
F(000)	1208	864
Crystal dimensions/mm	0.40×0.28×0.23	0.30×0.30×0.10
Scan range, θ/deg	1.55—25.00	10.45—22.21
Ranges of indices of measured reflections	$-13 \le h \le 9$	$-11 \le h \le 11$
	$-30 \le k \le 31$	$-11 \le k \le 11$
	$-13 \le l \le 12$	$-21 \le l \le 21$
Number of observed reflections	18062	12335
Number of independent reflections	5770	5184
R_{int}	0.0239	0.1763
Goodness-of-fit on F^2	0.913	0.873
R_1/wR_2 ($I > 2\sigma(I)$)	0.0370/0.0985	0.0689/0.1030
R_1/wR_2 (based on all reflections)	0.0451/0.1038	0.1806/0.1290
Residual electron density (ρ_{max}/ρ_{min})/e $Å^{-3}$	0.274/−0.152	0.186/−0.208

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecule **4**

Bond	*d*/Å	Angle	ω/deg
Mg(1)—O(2)	2.0257(11)	O(2)—Mg(1)—O(3)	96.62(4)
Mg(1)—O(3)	2.0267(11)	O(2)—Mg(1)—O(4)	90.02(4)
Mg(1)—O(4)	2.0415(10)	O(3)—Mg(1)—O(4)	79.80(4)
Mg(1)—O(1)	2.0440(10)	O(2)—Mg(1)—O(1)	79.61(4)
Mg(1)—O(6)	2.1067(11)	O(3)—Mg(1)—O(1)	94.57(4)
Mg(1)—O(5)	2.1242(11)	O(4)—Mg(1)—O(1)	167.61(4)
O(1)—C(1)	1.2771(17)	O(2)—Mg(1)—O(6)	167.95(5)
O(2)—C(6)	1.2750(17)	O(3)—Mg(1)—O(6)	91.86(5)
O(3)—C(15)	1.2781(17)	O(4)—Mg(1)—O(6)	99.92(4)
O(4)—C(20)	1.2806(17)	O(1)—Mg(1)—O(6)	91.23(4)
C(1)—C(2)	1.4355(19)	O(2)—Mg(1)—O(5)	96.20(4)
C(1)—C(6)	1.4825(19)	O(3)—Mg(1)—O(5)	164.47(5)
C(2)—C(3)	1.372(2)	O(4)—Mg(1)—O(5)	91.47(4)
C(3)—C(4)	1.424(2)	O(1)—Mg(1)—O(5)	96.33(4)
C(4)—C(5)	1.365(2)	O(6)—Mg(1)—O(5)	76.90(4)
C(5)—C(6)	1.4366(19)	C(1)—O(1)—Mg(1)	112.21(8)
C(15)—C(16)	1.439(2)	C(6)—O(2)—Mg(1)	112.50(9)
C(15)—C(20)	1.477(2)	C(15)—O(3)—Mg(1)	112.63(9)
C(16)—C(17)	1.366(2)	C(20)—O(4)—Mg(1)	111.94(9)
C(17)—C(18)	1.424(2)		
C(18)—C(19)	1.369(2)		
C(19)—C(20)	1.4399(19)		

coordination environment. The Mg(1) atom has a distorted octahedral environment formed by the O(2), O(3), O(4), and N(2) atoms lying in the base and the O(1) and N(1) atoms occupying the apical positions. The Mg(2) atom has a distorted tetrahedral environment. The vertices of the tetrahedron are occupied by the O(3), O(1), N(3), and N(4) atoms. In complex **8**, the Mg—O bond lengths are substantially different. The hexacoordinated Mg(1) atom is involved in two pairs of bonds, Mg(1)—O(2) and Mg(1)—O(4) (1.988(3) and 2.103(3) Å,

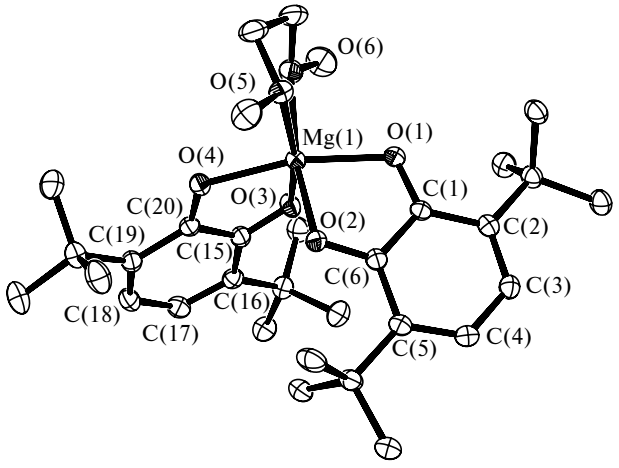


Fig. 2. Molecular structure of complex **4**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

Table 4. Selected bond lengths (*d*) and bond angles (ω) in molecule **8**

Bond	*d*/Å	Angle	ω/deg
Mg(1)—O(2)	1.988(3)	O(2)—Mg(1)—O(4)	153.88(14)
Mg(1)—O(4)	2.103(3)	O(2)—Mg(1)—O(1)	78.87(11)
Mg(1)—O(1)	2.123(3)	O(4)—Mg(1)—O(1)	78.92(12)
Mg(1)—O(3)	2.193(3)	O(2)—Mg(1)—O(3)	95.14(12)
Mg(1)—N(1)	2.198(4)	O(4)—Mg(1)—O(3)	71.56(11)
Mg(1)—N(2)	2.219(4)	O(1)—Mg(1)—O(3)	90.64(10)
Mg(2)—O(3)	1.939(3)	O(2)—Mg(1)—N(1)	93.21(14)
Mg(2)—O(1)	1.970(3)	O(4)—Mg(1)—N(1)	109.18(14)
Mg(2)—N(3)	2.045(5)	O(1)—Mg(1)—N(1)	171.90(14)
Mg(2)—N(4)	2.127(4)	O(3)—Mg(1)—N(1)	91.79(11)
Mg(2)—O(4)	2.517(3)	O(2)—Mg(1)—N(2)	100.00(14)
O(1)—C(1)	1.360(4)	O(4)—Mg(1)—N(2)	95.16(14)
O(2)—C(2)	1.327(4)	O(1)—Mg(1)—N(2)	94.20(12)
O(3)—C(15)	1.345(4)	O(3)—Mg(1)—N(2)	164.73(13)
O(4)—C(16)	1.368(5)	N(1)—Mg(1)—N(2)	85.42(13)
C(1)—C(6)	1.400(5)	O(3)—Mg(2)—O(1)	103.47(12)
C(1)—C(2)	1.430(6)	O(3)—Mg(2)—N(3)	102.90(17)
C(2)—C(3)	1.395(6)	O(1)—Mg(2)—N(3)	105.98(14)
C(3)—C(4)	1.384(6)	O(3)—Mg(2)—N(4)	120.46(13)
C(4)—C(5)	1.369(6)	O(1)—Mg(2)—N(4)	123.71(15)
C(5)—C(6)	1.405(6)	N(3)—Mg(2)—N(4)	97.11(18)
C(15)—C(20)	1.407(5)	O(3)—Mg(2)—O(4)	67.20(11)
C(15)—C(16)	1.416(6)	O(1)—Mg(2)—O(4)	72.38(10)
C(16)—C(17)	1.393(6)	N(3)—Mg(2)—O(4)	168.67(16)
C(17)—C(18)	1.386(6)	N(4)—Mg(2)—O(4)	92.89(14)
C(18)—C(19)	1.383(7)	Mg(2)—O(1)—Mg(1)	82.53(10)
C(19)—C(20)	1.387(6)	Mg(2)—O(3)—Mg(1)	81.41(10)
Mg(2)...C(39)	2.790(8)	Mg(1)—O(4)—Mg(2)	70.93(10)
Mg(1)...Mg(2)	2.702(2)		

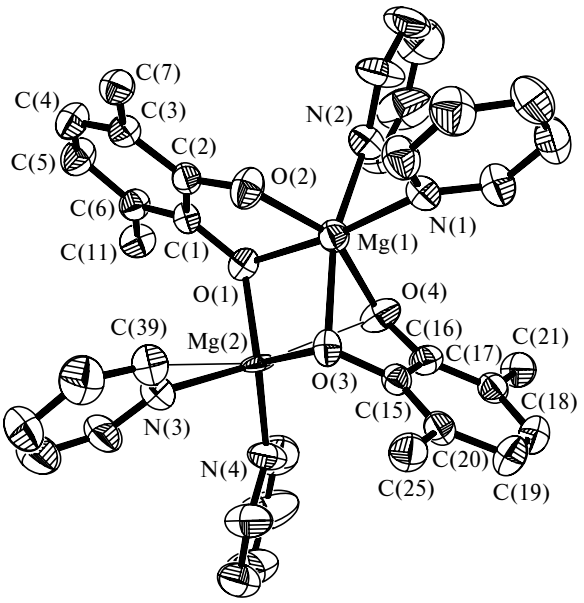


Fig. 3. Molecular structure of complex **8**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level. The hydrogen atoms and the methyl groups of the *tert*-butyl substituents are omitted.

respectively) and Mg(1)—O(1) and Mg(1)—O(3) (2.123(3) and 2.193(3) Å, respectively).

The Mg(2)—O(1), Mg(2)—O(3) (1.970(3), 1.939(3) Å) and Mg(2)—N(3), Mg(2)—N(4) (2.045(5), 2.127(4) Å) bonds are substantially shorter than the Mg(1)—O(2), Mg(1)—O(4) and Mg(1)—N(1), Mg(1)—N(2) bonds (2.198(4), 2.219(4) Å). This difference agrees well with the steric characteristics of the coordination spheres of the magnesium atoms. The degree of filling of the coordination sphere is lower and, consequently, nonbonded interactions between the ligands at the tetracoordinated Mg(2) atom are weaker compared to those at the hexacoordinated Mg(1) atom. As a result, the Mg(2)—O(N) distances are shorter than the analogous Mg(1)—O(N) bonds and, correspondingly, the degree of filling of the coordination sphere about the Mg(2) atom is higher. This fact is indirectly confirmed by the agostic Mg(2)...C(39) and Mg(2)...O(4) interactions. The Mg(2)...C(39) (2.790(8) Å) and Mg(2)...O(4) (2.517(3) Å) distances are substantially smaller than the sum of the van der Waals radii of these atoms.[36] This conclusion is in good agreement with a decrease in the covalent radii in tetracoordinated magnesium compounds compared to hexacoordinated compounds.[36]

In catecholate complex **8**, the C—O bond lengths (1.327(4)—1.368(5) Å) are substantially larger than the C—O bond lengths in complex **4** (1.2750(17)—1.2781(17) Å), which corresponds to reduction of *o*-benzosemiquinone to catechol. The dihedral angle between the planes of the catecholate ligands in complex **8** is 46.2°.

Therefore, excess amalgamated magnesium easily reduces *o*-quinone **1** in organic solvents to form metal complexes with *o*-quinone ligands in different oxidation states. In hydrocarbon solvents, magnesium bis-*o*-semiquinolate containing the coordinated unreduced *o*-quinone molecule is formed. If ethers are used as the reaction medium, the reaction stops at the formation of the compounds $SQ_2Mg \cdot L_n$ (L = DME or Et_2O; n = 1 or 2). The presence of solvents with a high coordinating ability (THF or pyridine) facilitates further reduction of magnesium bis-*o*-semiquinolates to bis-catecholate complexes containing two Mg^{2+} ions in different coordination environment.

Experimental

All experiments associated with the synthesis of magnesium catecholate and *o*-semiquinolate complexes were performed in the absence of traces of atmospheric oxygen and moisture.

The IR spectra were recorded on a FSM-1201 Fourier-transform spectrometer in Nujol mulls in KBr cells. The ESR spectra were measured on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT temperature controller. The ^{1}H NMR spectra were recorded on a Bruker DPX-200 Fourier-transform NMR spectrometer. The commercial solvents of reagent grade (*n*-hexane, toluene, THF, diethyl ether, dimethoxyethane, and pyridine) were purified and dried according to recommendations given in the study.[37] Quinone **1** was synthesized according to a known procedure.[38] Magnesium was amalgamated by treating magnesium with mercury(II) chloride in THF.[39]

[3,6-Di-(*tert*-butyl)-*o*-benzoquinone]bis[3,6-di-(*tert*-butyl)-*o*-benzosemiquinono]magnesium (2). A solution of *o*-quinone **1** (5.0 mmol, 1.10 g) in toluene (30 mL) was added to an excess of amalgamated magnesium (30.0 mmol, 0.72 g). The reaction mixture was vigorously stirred, which was accompanied by a change in the color of the mixture from red-green to dark-green and the formation of a dark-brown needle-like precipitate. The precipitate was dissolved on heating. The reaction mixture was stirred at 60 °C for 1 h. Then the solution was filtered off without cooling from the unconsumed metal on a glass filter No. 4. Cooling of the filtrate afforded finely crystalline complex **2**. The precipitate was filtered off, washed with cold hexane on the filter, and dried under reduced pressure. Analytically pure complex **2** was obtained in a yield of 0.94 g (83.0%). Found (%): C, 73.40; H, 8.61; Mg, 3.47. $C_{42}H_{60}O_6Mg$. Calculated (%): C, 73.62; H, 8.83; Mg, 3.55. IR, ν/cm^{-1}: 1640, 1502, 1475, 1446, 1383, 1365, 1355, 1275, 1233, 1202, 1178, 951, 822, 678, 654, 551, 495.

Synthesis of complexes 3 and 4. A solution of *o*-quinone **1** (5.0 mmol, 1.10 g) in diethyl ether (dimethoxyethane) (30 mL) was added to an excess of amalgamated magnesium (30.0 mmol, 0.72 g). The reaction mixture was vigorously stirred, which was accompanied by a change in the color of the mixture from red-green to dark-blue. Then the reaction mixture was vigorously stirred at room temperature for 1 h. The solution was separated from excess magnesium by filtration on a glass filter No. 4. The solution was concentrated under reduced pressure to one-third of the initial volume, and hexane (20 mL) was added to the residue. Crystals of complex **3** (in Et_2O) or **4** (in DME) precipitated on cooling. The resulting compounds are readily soluble in most of organic solvents, except for hexane. In the crystalline state, complexes **3** and **4** are stable to atmospheric oxygen. In solution, the complexes slowly decompose to give *o*-quinone.

Bis[3,6-di-(*tert*-butyl)-*o*-benzosemiquinono]magnesium bis(diethyletherate) (3). The yield was 1.31 g (85.8%). Blue crystals. Found (%): C, 70.41; H, 9.62; Mg, 4.10. $C_{36}H_{60}O_6Mg$. Calculated (%): C, 70.52; H, 9.86; Mg, 3.96. IR, ν/cm^{-1}: 1514, 1502, 1480, 1450, 1430, 1380, 1350, 1351, 1270, 1120, 1070, 950, 875, 840, 674, 655, 501, 490, 435.

Bis[3,6-di-(*tert*-butyl)-*o*-benzosemiquinono]magnesium dimethoxyethanate (4). The yield was 1.23 g (89.2%). Dark-blue crystals. Found (%): C, 69.21; H, 8.92; Mg, 4.03. $C_{32}H_{50}O_6Mg$. Calculated (%): C, 69.25; H, 9.08; Mg, 4.38. IR, ν/cm^{-1}: 1515, 1502, 1480, 1448, 1389, 1363, 1351, 1276, 1240, 1200, 1180, 1115, 1070, 952, 876, 825, 674, 655, 540, 490, 445.

Synthesis of complexes 7 and 8. A solution of *o*-quinone **1** (5.0 mmol, 1.10 g) in tetrahydrofuran (pyridine) (30 mL) was added to an excess of amalgamated magnesium (30.0 mmol, 0.72 g). The reaction mixture was vigorously stirred at 60 °C. The color of the reaction mixture changed from red-green to dark-blue in a few minutes. After further stirring for 1 h, the reaction mixture turned pale-yellow. The solution was separated from excess magnesium by filtration on a glass filter No. 4.

Bis[3,6-di-(*tert*-butyl)catecholato]dimagnesium tetrakis-tetrahydrofuranate (7). Tetrahydrofuran was removed under reduced pressure, and the residue was recrystallized from hot hexane. White crystalline complex **7** was obtained in a yield of 1.47 g (75.8%). Found (%): C, 68.21; H, 9.52; Mg, 6.13. $C_{22}H_{36}O_4Mg$. Calculated (%): C, 67.96; H, 9.33; Mg, 6.25. ^{1}H NMR (200 MHz, $CDCl_3$, 20 °C), δ: 6.82 (s, 2 H, H_{arom}); 3.57 (s, 8 H, H_α (THF)); 1.67 (s, 8 H, H_β (THF)); 1.38 (s, 18 H, Bu^t). IR, ν/cm^{-1}: 1460, 1275, 1260, 1250, 1225, 1185, 1050, 975, 912, 710, 650.

Bis[3,6-di-(*tert*-butyl)catecholato]bis-pyridinedimagnesium (8). The resulting pyridine solution was concentrated to one-half of the initial volume. Yellow crystals of complex **8** precipitated on cooling. The yield was 1.72 g (85.4%). Found (%): C, 71.68; H, 7.74; Mg, 5.89. $C_{48}H_{60}O_4N_4Mg_2$. Calculated (%): C, 71.56; H, 7.51; Mg, 6.03. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 20 °C), δ: 8.56 (s, 4 H, H_α (Py)); 7.73 (s, 2 H, H_γ (Py)); 7.35 (s, 4 H, H_β (Py)); 6.71 (s, 2 H, H_{arom}); 1.36 (s, 18 H, Bu^t). IR, ν/cm^{-1}: 1607, 1425, 1280, 1265, 1240, 1220, 1145, 1070, 1040, 975, 935, 755, 700, 665.

X-ray diffraction study. X-ray diffraction studies were performed on a Smart Apex diffractometer (Mo-Kα, graphite monochromator). The structures of complexes **4** and **8** were solved by direct methods and refined by the full-matrix least-squares method against F^2 with the use of the SHELXTL program package.[40] Absorption corrections were applied using the SADABS program.[41] All nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms in complex **4** were located in difference electron density maps and refined isotropically. The positions of the hydrogen atoms in complex **8** were placed in geometrically calculated positions and refined using a riding model.

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References

1. C. Pettinari, F. Marchetti, and A. Drodzov, in *Comprehensive Coordination Chemistry II,* Eds J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, Vol. **1**, p. 91.
2. C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216/217**, 99.
3. D. A. Shultz, in *Magnetism: Molecules to Materials II*, Eds J. S. Miller and M. Drillon, Wiley—VCH, Weinheim—New York, 2002, p. 281.
4. A. Dei, D. Gatteschi, C. Sangregorio, and L. Sorace, *Acc. Chem. Res.*, 2004, **37**, 827.
5. I. N. Markevtsev, M. P. Monakhov, V. V. Platonov, A. S. Mischenko, A. K. Zvezdin, M. P. Bubnov, G. A. Abakumov, and V. K. Cherkasov, *J. Magnetism and Magnetic Materials*, 2006, **300**, e407.
6. O. Sato, *J. Photochem. Photobiol. C, Photochem. Rev.*, 2004, **5**, 203.
7. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, V. A. Kuropatov, G. T. Yee, and C. G. Pierpont, *Inorg. Chem.*, 2001, **40**, 2434.
8. M. I. Kabachnik, N. N. Bubnov, A. I. Prokof´ev, and S. P. Solodovnikov, *Science Rev., B*, 1981, **3**, 197.
9. V. K. Cherkasov, G. A. Abakumov, E. V. Grunova, A. I. Poddel´sky, G. K. Fukin, E. V. Baranov, Y. A. Kurskii, and L. G. Abakumova, *Chem. Eur. J.*, 2006, **12**, 3916.
10. A. V. Lado, A. I. Poddel´sky, A. V. Piskunov, G. K. Fukin, E. V. Baranov, V. N. Ikorskii, V. K. Cherkasov, and G. A. Abakumov, *Inorg. Chim. Acta*, 2005, **358**, 4443.
11. G. A. Abakumov, A. I. Poddel´sky, E. V. Grunova, V. K. Cherkasov, G. K. Fukin, Y. A. Kurskii, and L. G. Abakumova, *Angew. Chem., Int. Ed.*, 2005, **44**, 2767.
12. A. V. Piskunov, I. A. Aivaz´yan, G. K. Fukin, E. V. Baranov, A. S. Shavyrin, V. K. Cherkasov, and G. A. Abakumov, *Inorg. Chem. Commun.*, 2006, **9**, 612.
13. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2003, 3336.
14. I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, and M. P. Bubnov, *Inorg. Chem.*, 2004, **43**, 7807.
15. H. Schumann, M. Hummert, A. N. Lukoyanov, and I. L. Fedushkin, *Organometallics*, 2005, **24**, 3891.
16. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, V. K. Cherkasov, G. K. Fukin, and M. A. Lopatin, *Eur. J. Inorg. Chem.*, 2004, 388.
17. A. V. Lado, A. V. Piskunov, V. K. Cherkasov, G. K. Fukin, and G. A. Abakumov, *Koord. Khim.,* 2006, **32**, 181 [*Russ. J. Coord. Chem.*, 2006, **32**, 173 (Engl. Transl.)].
18. B. Tumanskii, P. Pine, Y. Apeloig, N. J. Hill, and R. West, *J. Am. Chem. Soc.*, 2004, **126**, 7786.
19. B. Tumanskii, P. Pine, Y. Apeloig, N. J. Hill, and R. West, *J. Am. Chem. Soc.*, 2005, **127**, 8248.
20. G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, I. A. Aivaz´yan, and N. O. Druzhkov, *Dokl. Akad. Nauk*, 2005, **404**, 496 [*Dokl. Chem.*, 2005, **404**, 189 (Engl. Transl.)].
21. A. V. Piskunov, I. A. Aivaz´yan, V. K. Cherkasov, and G. A. Abakumov, *J. Organomet. Chem.*, 2006, **691**, 1531.
22. I. L. Fedushkin, A. A. Skatova, A. N. Lukoyanov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2641 [*Russ. Chem. Bull., Int. Ed.*, 2004, **54**, 2751].
23. I. L. Fedushkin, V. M. Makarov, E. C. E. Rosenthal, and G. K. Fukin, *Eur. J. Inorg. Chem.*, 2006, 827.
24. I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, and G. K. Fukin, *Chem. Eur. J.*, 2005, **11**, 5749.
25. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Chem. Eur. J.*, 2003, **9**, 5778.
26. A. V. Piskunov, S. V. Maslennikov, I. V. Spirina, and V. P. Maslennikov, *Koord. Khim.,* 2002, **28**, 861 [*Russ. J. Coord. Chem.*, 2002, **28**, 808 (Engl. Transl.)].
27. A. Ozarowsky, B. R. McGarvey, C. Peppe, and D. G. Tuck, *J. Am. Chem. Soc.*, 1991, **113**, 3288.
28. S. V. Maslennikov, E. N. Kirillov, N. V. Berezina, I. V. Spirina, and A. V. Kondin, *Zh. Obshch. Khim.*, 1997, **67**, 714 [*Russ. J. Gen. Chem.*, 1997, **67**, 667 (Engl. Transl.)].
29. A. V. Piskunov, S. V. Maslennikov, V. K. Cherkasov, I. V. Spirina, and V. P. Maslennikov, *Zh. Obshch. Khim.*,

2002, **72**, 997 [*Russ. J. Gen. Chem.*, 2002, **72**, 933 (Engl. Transl.)].
30. C. W. Lange and C. G. Pierpont, *Inorg. Chim. Acta*, 1997, **263**, 219.
31. A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance, with Applications to Chemistry and Chemical Physics,* Harper and Row, New York—London, 1967, 266 pp.
32. N. A. Malysheva, A. I. Prokof´ev, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 997 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28** (Engl. Transl.)].
33. C. A. Zechmann, T. J. Boyle, M. A. Rodriguez, and R. A. Kemp, *Polyhedron*, 2000, **19**, 2557.
34. T. Hatanpalal, J. Kansikas, I. Mutikainen, and M. Leskelal, *Inorg. Chem.*, 2001, **40**, 788.
35. C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
36. S. S. Batsanov, *Zh. Neorg. Khim.,* 1991, **36**, 3015 [*Russ. J. Inorg. Chem.*, 1991, **36**, 1694 (Engl. Transl.)].
37. A. J. Gordon and R. A. Ford, *The Chemist´s Companion*, Wiley Interscience Publication, New York, 1972, 537 pp.
38. V. A. Garnov, V. I. Nevodchikov, L. G. Abakumova, G. A. Abakumov, and V. K. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1863 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1728 (Engl. Transl.)].
39. S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Am. Chem. Soc.*, 1973, **95**, 4469.
40. G. M. Sheldrick, *SHELXTL v. 6.12, Structure Determination Software Suite,* Bruker AXS, Madison, Wisconsin, USA, 2000.
41. G. M. Sheldrick, *SADABS v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA, 1998.

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