# New lead(II) catecholate and *o*-semiquinone complexes

G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, \* A. V. Lado, 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: pial@iomc.ras.ru

Lead(II) catecholate complexes were prepared by reduction of 3,6-di-*tert*-butyl-o-benzoquinone and its derivatives with lead metal in THF. The molecular structure of the (CatPb)<sub>4</sub>·(PbO)<sub>2</sub>· $6C_3H_6O$  complex (Cat is the dianion of 3,6-di-*tert*-butylcatechol), which was synthesized by hydrolysis of lead 3,6-di-*tert*-butylcatecholate in acetone, was established by X-ray diffraction. A series of lead(II) o-semiquinone complexes, which were prepared by the addition of the phenoxyl radical to lead catecholates or by oxidation of the latter with mercury(II), copper(II), or silver(I) halides, were studied by the ESR method. Lead(II) monoo-semiquinolate complexes undergo symmetrization to form stable bis-o-semiquinolates, which were isolated and characterized in individual state.

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

Among complexes of *p*-block metals, lead(II) compounds are of particular interest for coordination chemistry. Lead(II) equally readily form complexes with both hard and soft bases, the coordination number of the metal varying from 2 to  $8.^1$  Due to considerable coordination capabilities, the chemistry of lead(II) is very attractive but poses additional problems for researchers. The coordination spheres of metals (true coordination number, the geometry of substituents at the central atom, the equilibrium, and the ligand exchange mechanism) are studied by the spin-label method<sup>2</sup> applied to both transition<sup>3-6</sup> and main-group metals.<sup>7–8</sup> The radical anions of sterically hindered o-quinones are among the most widely used spin-labeled ligands. In this connection, the synthesis of o-quinone lead(II) complexes and study of these complexes by the ESR method hold considerable promise.

Only a few *o*-quinone lead(II) complexes are known. The formation of polymeric lead(II) 3,5-di-*tert*-butyl-catecholate in the course of oxidation of tetraethyllead with 3,5-di-*tert*-butyl-*o*-benzoquinone (1) was documented.<sup>9</sup> Lead metal reacts with compound 1 in various aprotic solvents to give exclusively polymeric lead(II) catecholate, which is poorly soluble in most of organic solvents.<sup>10</sup> Lead(II) bis-phenanthrenesemiquinolate was synthesized by refluxing a lead wire with phenanthrene-quinone in hexane.<sup>11</sup>

In the present study, we synthesized lead(II) catecholate complexes by reduction of 3,6-di-*tert*-butylo-benzoquinone (2) and its derivatives, viz., 3,6-di-*tert*butyl-4-methoxy-o-benzoquinone (3) and 3,6-di-*tert*butyl-4-chloro-o-benzoquinone (4), with lead metal in THF and investigated the redox reactions with the resulting compounds.

## **Results and Discussion**

One of the most widely used methods for the synthesis of o-quinone metal complexes is based on metathesis reactions of catecholate and o-semiquinolate derivatives of alkali metals or thallium with metal halides.<sup>12</sup> However, because of poor solubility of lead(II) halides, direct oxidation of this metal with o-quinones is a method of choice. This method is commonly used for the synthesis of o-quinone complexes of main-group metals.<sup>13</sup>

Reduction of *o*-quinones **2**–**4** with excess lead metal in a THF solution occurs stepwise. In the first step, the initial red color of *o*-quinone disappears and the reaction mixture turns green. These changes are accompanied by the appearance of the ESR spectrum. The isotropic ESR spectra of the reaction mixtures are complex superpositions of different signals. In the initial step, the ESR spectra are observed regardless of the nature of o-quinone involved in the reaction with metal. These spectra correspond to the free o-semiguinone radical anions  $(g_i = 2.0041, a_i(2H) = 0.35 \text{ mT}; g_i = 2.0045, a_i(3H) =$ 0.05 mT,  $a_i(H) = 0.39$  mT;  $g_i = 2.0055$ ,  $a_i(^{35,37}Cl) =$ 0.05 mT,  $a_i(H) = 0.33$  mT for *o*-quinones **2**, **3**, and **4**, respectively). In addition, the ESR spectra show signals belonging to mono-o-semiquinone derivatives of lead, as evidenced by satellite splitting on the <sup>207</sup>Pb magnetic isotopes (22.1%, I = 1/2,  $\mu_N = 0.5926$ ).<sup>14</sup> The ESR parameters of the paramagnetic compounds are as follows:  $g_i = 2.0018$ ,  $a_i(2H) = 0.35$  mT,  $a_i(^{207}Pb) = 7.95$  mT;  $g_i = 1.9998$ ,  $a_i(2H) = 0.35$  mT,  $a_i(^{207}Pb) = 6.03$  mT;  $g_i = 1.9990, a_i(2H) = 0.35 \text{ mT}, a_i(2H) = 0.05 \text{ mT}, a_i(207 \text{Pb}) = 5.01 \text{ mT} \text{ for}$  *o*-quinone **2**;  $g_i = 2.0015, a_i(3H) = 0.05 \text{ mT}, a_i(H) = 0.39 \text{ mT}, a_i(207 \text{Pb}) = 7.14 \text{ mT}; g_i = 1.9997, a_i(3H) = 0.05 \text{ mT}$ 

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0.05 mT,  $a_i(H) = 0.39$  mT,  $a_i(^{207}Pb) = 5.46$  mT;  $g_i =$ 1.9989,  $a_i(3H) = 0.05 \text{ mT}$ ,  $a_i(H) = 0.39 \text{ mT}$ ,  $a_i(^{207}\text{Pb}) =$ 4.41 mT for *o*-quinone **3**;  $g_i = 2.0004$ ,  $a_i(^{35,37}Cl) = 0.05$  mT,  $a_i(H) = 0.33$  mT,  $a_i(^{207}Pb) = 5.04$  mT;  $g_i = 1.9999, a_i(^{35,37}\text{Cl}) = 0.05 \text{ mT}, a_i(\text{H}) = 0.33 \text{ mT},$  $a_i(^{207}\text{Pb}) = 4.52 \text{ mT}$  for o-quinone 4. The g factors (1.9990-2.0018) and the hyperfine coupling constants with the lead magnetic isotope  $a_i$ <sup>(207</sup>Pb) (4.41-7.95 mT) unambiguously indicate that the resulting compounds are paramagnetic lead(II) complexes. The ESR parameters observed in the course of the reaction substantially differ from those obtained earlier for o-semiguinone (SQ) derivatives of lead(IV). The latter are characterized by higher g factors  $(2.0022-2.0044)^9$  and substantially lower hyperfine coupling constants  $a_i$  (<sup>207</sup>Pb) (0.90-0.93 mT).<sup>9</sup> The observed differences are also characteristic of thallium(1)<sup>15</sup> and thallium(III)<sup>16</sup> o-semiquinolates and have been discussed in detail in the studies.<sup>9,16</sup>

The presence of several signals belonging to monoo-semiquinone derivatives of lead(II) in the ESR spectra measured in the early step of the reaction is apparently attributed to dissolution of an oxide film from the surface of the metal involved in the reaction. This should lead to the appearance of SQPb-OH, SQPb-O-Pb,  $[SQPb]^+ \cdot THF$ , etc. compounds in solution. The same conclusion has been drawn by researchers, who studied reduction of o-quinone 1 with tin,<sup>17</sup> magnesium,<sup>18,19</sup> zinc,<sup>20</sup> and cadmium<sup>19,20</sup> by ESR spectroscopy and observed the formation of mono-o-semiquinone derivatives of metals. The presence of noncoordinated semiguinone radical anions in the reaction mixture is indicative of the presence of solvent-separated ion pairs in solution.<sup>21</sup> These data are consistent with the results of ESR studies of the reaction of lead metal with *o*-quinone 1.<sup>10,11</sup>

The reaction is accompanied by the appearance of the intense blue color, and the components of the isotropic ESR spectrum become strongly broadened. In this step, the anisotropic ESR spectra of the reaction mixtures in a 2-methyltetrahydrofuran matrix are superpositions of a singlet and signals characteristic of biradical species (Fig. 1). The ESR spectra have also a half-field singlet ( $H \approx 1700$  G) corresponding to the transition  $\Delta m_s = 2$ . The zero-field splitting constants and the average dis-



Fig. 1. Anisotropic spectrum of the reaction mixture prepared by reduction of *o*-quinone **4** with lead metal (2-methyltetra-hydrofuran, T = 130 K).

Table 1. Zero-field splitting parameters and the average distances between the radical centers in biradical lead derivatives 5-7

| Complex | $ D_{\parallel} $ | E   | <i>r/</i> Å |
|---------|-------------------|-----|-------------|
|         | (                 | Ĵ   |             |
| 5       | 368               | 9.0 | 5.3         |
| 6       | 316               | 6.0 | 5.6         |
| 7       | 334               | 7.5 | 5.5         |

tances between the radical centers calculated in the dot—dipole approximation<sup>2</sup> for the resulting biradicals are given in Table 1.

These ESR spectra provide evidence for the formation of the corresponding bis-*o*-semiquinone metal complexes 5-7 in the reactions of *o*-quinones 2-4 with lead metal (Scheme 1).

The further contact of the reaction mixture with excess lead leads to a change in the color to yellow and the disappearance of the ESR signal. After completion of the reaction, one mole of the metal was consumed per mole of *o*-quinone involved in the reaction. The resulting lead complexes can be isolated from a THF solution as yellow finely crystalline precipitates by the addition of toluene or hexane. The characteristic sets of bands in the 700–1600 cm<sup>-1</sup> region of the IR spectra and elemental analysis data for the reaction products indicate that the reactions afford the corresponding catecholate derivatives of lead(II) **8–10** (see Scheme 1).





R = H (2, 5, 8), MeO (3, 6, 9), Cl (4, 7, 10)

The resulting compounds are insoluble in acyclic ethers, hydrocarbons, their chloro derivatives, and nitrogen-containing solvents (pyridine, acetonitrile, and amines) but are readily soluble in THF, dioxane, and dimethoxyethane, as well as in acetone on heating. The complexes isolated from THF solutions (IR spectroscopic data) contain no coordinated solvent molecules. In the crystalline state, compounds 8-10 exist apparently as coordination polymers. The latter can be formed through additional bridging Pb-O-Pb bonds involving the oxygen atoms of the catecholate ligands. This behavior is characteristic of oxygen-containing divalent lead complexes.<sup>1</sup> The same conclusion was drawn in the studies, where lead(II) catecholate was synthesized starting from o-quinone 1.<sup>10,11</sup> The presence of sterically nonshielded oxygen atom at position 1 of o-quinone 1 results in even lower solubility of the resulting complex compared to compounds 8-10.

In the study of lead(II) carboxylates, it was demonstrated<sup>23</sup> that such coordination polymers can be transformed into lead(II) oxide-containing clusters by partial hydrolysis. We found that hydrolysis of compound **8** by refluxing in acetone containing ~1% of water afforded the new lead complex, tetrakis(3,6-di-*tert*-butylcatecholato)bis( $\mu_4$ -oxo)hexalead(II) hexakis(acetone) solvate (**11**) (Scheme 2, the acetone molecules in the structural formula of complex **11** are omitted).



This compound is an example of hybrid "metal-organic framework" complexes. The chemistry of these complexes has been extensively developed in recent years because they are promising reagents in chemistry and technology.<sup>24</sup>

X-ray diffraction study demonstrated that **11** is a centrosymmetric complex formed through the Pb–O donor-



**Fig. 2.** Molecular structure of complex **11**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The H atoms, the *tert*-butyl groups, and the acetone molecules (except for the O(1s) and O(2s) atoms involved in coordination with the lead atoms) are omitted.

acceptor bonds and consists of the PbO dimer, in which the Pb(3)O(5) and Pb(3A)O(5A) fragments are additionally coordinated by two lead(II) catecholate molecules through the oxygen atoms (Fig. 2). Selected bond lengths and bond angles are given in Table 2. The catecholate fragments are differently arranged relative to the PbO dimer (Fig. 3). There is only one donor-acceptor bond,



Fig. 3. Fragments A (*a*) and B (*b*) of the structure of complex 11. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The H atoms and the acetone molecules are omitted.

Table 2. Selected bond lengths (d) and bond angles ( $\omega$ ) in complex 11

Pb(1)–O(5), between the catecholate metallocycle and the PbO dimer in the fragment **A** (see Fig. 3, *a*). In the fragment **B** (see Fig. 3, *b*), there are three such interactions, Pb(2)–O(5), Pb(3)–O(3), and Pb(3A)–O(4). The dihedral angle between the Pb(2)O(3)O(4) and Pb(3)O(5)Pb(3A)O(5A) planes is  $8.5^{\circ}$ .

The Pb(1)-O(5) distance (2.291(3) Å) in the fragment A is substantially larger than the endocyclic Pb(1)-O(1) and Pb(1)-O(2) bond lengths (2.212(3) and 2.228(3) Å, respectively) in the five-membered metallocycle but is comparable with the analogous distances in lead(II) oxide (2.256(3) and 2.291(3) Å). In the fragment **B**, the Pb(2)-O(5), Pb(3)-O(3), and Pb(3A) - O(4) distances (2.349(3), 2.554(3), and 2.548(3) Å, respectively) are substantially longer than the analogous distance in A. In addition, the Pb(2)-O(3) and Pb(2)-O(4) distances (2.278(3) and 2.284(3) Å) in the catecholate moiety of the fragment **B** are also substantially longer than the analogous distances in A and are comparable with the Pb(1)-O(5) bond length. The O-Cdistances in the catecholate metallocycles of the fragments A and B of complex 11 are equal within experimental error (1.345(5)-1.376(5) Å) and are in the range characteristic of this type of ligands.<sup>12</sup>

Unlike the fragment **A**, in which the catecholate metallocycle is virtually planar, the fragment **B** is folded along the O(3)...O(4) line (28.0°) away from the Pb(1) and Pb(1A) atoms. Apparently, the folding along the O(3)...O(4) line is attributed to steric effects in the complex. If the fragment **B** were planar, substantial nonbonded

repulsions would occur between all components of complex 11.

In the molecule of complex 11, there is an interaction between the Pb(1) atom and the aromatic system of the catecholate ligand C(15)–C(20). It should be noted that the average Pb(1)–C(15–20) distance in molecule 11 (3.49 Å) is substantially longer than the average Pb–C(arom.) distance (3.20 Å) in lead(II) bis(( $\eta^6$ -o-xylene)tetrachloroaluminate),<sup>25</sup> which is the only known compound with  $\eta^6$  coordination of the aromatic system to lead(II).

The lead atoms in molecule **11** form a distorted octahedron with the Pb(1)Pb(2)Pb(1A)Pb(2A) base and the vertices occupied by the Pb(3) and Pb(3A) atoms. This cluster can alternatively be described by two edge-sharing tetrahedra. The  $\mu_4$ -oxo ligands O(5) and O(5A) are located in the centers of the tetrahedra. An analogous core, Pb<sub>6</sub>O<sub>2</sub>, was found in the compound produced by the hydrothermal synthesis of lead(II) benzoylbenzoate.<sup>23</sup>

Complex **11** contains also six acetone molecules. These molecules are arranged in three equivalent pairs relative to the lead atoms. It should be noted that one pair does not form donor-acceptor bonds with the metal atom. In two other pairs, the Pb–O distances are in the range of 2.819(3)–3.221(3) Å, which is indicative of coordination interactions. The O(1s) and O(2s) atoms of two non-equivalent coordinated acetone molecules are shown in Fig. 2. One acetone molecule (O(1s)) is coordinated to the Pb(2) atom, and the other molecule (O(2s)) forms donor-acceptor bonds with all three lead atoms,



 $\mathsf{R}=\mathsf{H}\ (\mathbf{8},\ \mathbf{12},\ \mathbf{15},\ \mathbf{16},\ \mathbf{19},\ \mathbf{22},\ \mathbf{25}),\ \mathsf{MeO}\ (\mathbf{9},\ \mathbf{13},\ \mathbf{17},\ \mathbf{20},\ \mathbf{23},\ \mathbf{26}),\ \mathsf{Cl}\ (\mathbf{10},\ \mathbf{14},\ \mathbf{18},\ \mathbf{21},\ \mathbf{24},\ \mathbf{27})$ 

Pb(1)—Pb(3). Therefore, taking into account the lone electron pairs of the metal atoms occupying the vacancies in the coordination environment, the lead atoms have the following coordination numbers (coordination polyhedra): Pb(1), 4 (distorted tetragonal pyramid); Pb(2), 6 (distorted monocapped trigonal prism); Pb(3), 5 (distorted octahedron).

Complex 11, unlike compounds 8-10, is much more readily soluble and can be recrystallized, for example, from hot toluene.

Compounds 8-10 in a THF solution are very sensitive to oxidizing agents, due to which they can be used for the preparation of various *o*-semiquinone derivatives of lead(II) (Scheme 3).

Oxidation of lead catecholates 8-10 with *o*-quinones 2-4 affords the corresponding bis-*o*-semiquinone derivatives 5-7. The parameters of the anisotropic ESR spectra of the latter are identical to those observed in the course of reduction of *o*-quinones with lead (see Table 1). Complexes 5 and 6 were isolated in individual state by recrystallization from hexane. Compound 7 gradually decomposes in solution to form lead(II) chloride.

Oxidation of catecholates 8-10 with copper(II), mercury(II), and silver(I) salts, molecular iodine, and ben-

zoyl peroxide in THF solutions generate new three-coordinate mono-*o*-semiquinone lead(II) complexes. The ESR spectra of the resulting compounds reveal interactions of the unpaired electron with the magnetic nuclei of the *o*-semiquinone ligand and the <sup>207</sup>Pb magnetic isotope. For derivatives **12–18**, the hyperfine coupling constants with the magnetic isotopes of the halogen atoms are also observed (Fig. 4). The ESR parameters of the resulting complexes are given in Table 3.

It was reported<sup>9</sup> that lead(iv) diethylcatecholate can add the phenoxyl radical to give the corresponding *o*-semiquinone derivative. The addition of stable 3,6-di-*tert*-butyl-2-ethoxyphenoxyl to solutions of compounds **8**–**10** leads to the disappearance of the ESR signal of the starting aroxyl radical and the appearance of new spectra (Fig. 5), which are indicative of the formation of *o*-semiquinone lead(ii) complexes **19–21**.

Complexes 12–27 are the first lead derivatives in the series of three-coordinate complexes of divalent 14 Group elements containing paramagnetic ligands. Analogous derivatives of silicon,<sup>26</sup> germanium,<sup>27–29</sup> and tin<sup>8,30</sup> were documented known. The (BIAN)GeCl complex (BIAN is the *N*,*N*-substituted acenaphthenediimine radical anion) was studied by X-ray diffraction<sup>27</sup> and it was demon-

Scheme 3

| Com- | $g_{\mathrm{i}}$ | <i>a</i> <sub>i</sub> (H) (1 H) | $a_{i}(R)$   | $a_{\rm i}(^{207}{\rm Pb})$ | a <sub>i</sub> (Hal)                                 |  |  |
|------|------------------|---------------------------------|--|-----------------------------|--|--|--|
| plex |                  |                                 | mT   |                             |  |  |  |
| 12   | 2.0002           | 0.345                           | 0.345 (1 H)  | 6.240                       | 0.150 ( <sup>35</sup> Cl), 0.125 ( <sup>37</sup> Cl) |  |  |
| 13   | 2.0003           | 0.385                           | 0.055 (3 H)  | 5.380                       | 0.147 ( <sup>35</sup> Cl), 0.128 ( <sup>37</sup> Cl) |  |  |
| 14   | 2.0012           | 0.335                           | 0.060 ( <sup>35</sup> Cl), 0.050 ( <sup>37</sup> Cl) | 5.720                       | 0.145 ( <sup>35</sup> Cl), 0.120 ( <sup>37</sup> Cl) |  |  |
| 15   | 2.0032           | 0.325                           | 0.325 (1 H)  | 6.850                       | 0.890( <sup>127</sup> I)                             |  |  |
| 16   | 2.0011           | 0.350                           | 0.350 (1 H)  | 6.080                       | 0.690 ( <sup>79</sup> Br), 0.750 ( <sup>81</sup> Br) |  |  |
| 17   | 2.0009           | 0.380                           | 0.060 (3 H)  | 5.390                       | 0.670 ( <sup>79</sup> Br), 0.720 ( <sup>81</sup> Br) |  |  |
| 18   | 2.0024           | 0.330                           | 0.060 ( <sup>35</sup> Cl), 0.050 ( <sup>37</sup> Cl) | 5.610                       | 0.670 ( <sup>79</sup> Br), 0.720 ( <sup>81</sup> Br) |  |  |
| 19   | 2.0015           | 0.347                           | 0.347 (1 H)  | 7.540                       |  |  |  |
| 20   | 2.0011           | 0.370                           | 0.050 (3 H)  | 6.800                       |  |  |  |
| 21   | 2.0008           | 0.330                           | 0.045 ( <sup>35</sup> Cl), 0.037 ( <sup>37</sup> Cl) | 5.350                       |  |  |  |
| 22   | 1.9960           | 0.355                           | 0.355 (1 H)  | 2.130                       |  |  |  |
| 23   | 1.9961           | 0.380                           | 0.050 (3 H)  | 1.760                       |  |  |  |
| 24   | 1.9971           | 0.350                           | 0.055 ( <sup>35</sup> Cl), 0.045 ( <sup>37</sup> Cl) | 2.120                       |  |  |  |
| 25   | 1.9998           | 0.350                           | 0.350 (1 H)  | 5.820                       |  |  |  |
| 26   | 1.9994           | 0.380                           | 0.055 (3 H)  | 5.180                       |  |  |  |
| 27   | 2.0006           | 0.345                           | 0.055 ( <sup>35</sup> Cl), 0.045 ( <sup>37</sup> Cl) | 5.230                       |  |  |  |

Table 3. ESR parameters of lead *o*-semiquinone derivatives 12–27



**Fig. 4.** Experimental (*a*) and calculated (*b*) ESR spectra of complex **12** in THF (T = 290 K).



Fig. 5. ESR spectrum of complex 19 in THF (T = 290 K).

strated that the structure of this complex can be described as a distorted trigonal pyramid, whose base is formed by two nitrogen atoms and the chlorine atom and the apex is occupied by the lone electron pair of the germanium atom. Based on the ESR parameters of the derivatives LSnCl and LGeCl (L is the radical anions of the diazabutadiene series), the trigonal-pyramidal geometry was proposed also

in the studies.<sup>8,28,30</sup> Analogous structures were also typical of the known three-coordinate lead(II) complexes.<sup>31,32</sup> Similar trigonal structures would be expected for complexes 12-27.



This is also evidenced by the ESR parameters of halide complexes **12–18**. The high hyperfine coupling constants with the magnetic isotopes of the halogen atoms indicate that the  $\sigma(\sigma^*)$  orbitals of Pb-Hal make a substantial contribution to  $\pi$ -MO occupied by the unpaired electron. This interaction is favored by the geometry of complexes in which the Pb–Hal bonds are orthogonal to the plane of the metallocycle. The hyperfine coupling constants  $a_i(^{35,37}\text{Cl})$  for the paramagnetic three-coordinate complexes decrease in the Ge–Sn–Pb series (0.9–1.1 mT <sup>27,28</sup> > 0.5–0.7 mT <sup>8,30</sup> > 0.14–0.15 mT) with the simultaneous increase in the ionic radius of the divalent elements (0.90 Å > 0.93 Å > 1.32 Å),<sup>14</sup> which is also consistent with the proposed geometry.

The hyperfine coupling constants  $a_i(^{207}\text{Pb})$  and the *g* factors for the ESR spectra of complexes **12–27** vary in a wide range, whereas the hyperfine coupling constants with the magnetic nuclei of the *o*-semiquinone ligand are virtually equal within experimental error (see Table 3). Taking into account the proposed geometry of the lead

o-semiquinone complexes, it can be stated that the formation of o-semiquinone complexes is accompanied by hybridization of the occupied 6s orbital and the unoccupied 6p orbital of lead to form a distorted tetrahedral coordination sphere. The vertices are occupied by the oxygen atoms, the substituent X, and the lone electron pair of lead. In this case, the s orbital, which has a nonzero density on the metal nucleus, makes a substantial contribution to the orbitals, which can directly interact with the orbital of the unpaired electron. This results in an additional large contribution to the hyperfine coupling constants without changes in the spin density of the ligand. According to the proposed mechanism, excitation of the lone electron pair to the  $\pi_{SO}^*$  molecular orbital should cause an increase in the g factor with a simultaneous increase in the hyperfine coupling constant on the lead magnetic isotope,  $a_i(^{207}\text{Pb})$ . This dependence is clearly seen among related (closest environment of the lead atom consists of three oxygen atoms) lead o-semiquinolate complexes 19–27, including paramagnetic lead derivatives observed in the course of reduction of o-quinones with metal (Fig. 6).

The g factor increases according to the equation

 $\Delta g = 2\lambda/\Delta E$ ,

where  $\lambda$  is the spin-orbital coupling constant and  $\Delta E$  is the energy difference between the  $\pi_{SQ}^*$  molecular orbital occupied by the unpaired electron and MO occupied by the lone electron pair of the metal atom (Fig. 7).

The effective positive charge of the lead atom in complexes containing more electronegative substituents X is higher compared to that in compounds containing less electronegative substituents, which, in turn, results in an increase in the MO level occupied by the lone electron pair and an increase in the g factor. As an example, the relative changes in the energy of MO of the triflate (**22**) and phenolate (**19**) lead o-semiquinone complexes are presented in Fig. 7.



**Fig. 6.** Plots  $g_i - a_i(^{207}\text{Pb})$  for lead(11) *o*-semiquinone complexes derived from *o*-quinones **2** (*1*), **3** (*2*), and **4** (*3*).



Fig. 7. Molecular orbital diagram for lead *o*-semiquinone complexes **19** and **22**.

Due to the ability of catecholate derivatives of lead(II) to add O-centered radicals, compounds **8**–10 can be used as spin traps for this type of radicals. The strong dependence of the ESR parameters for lead(II) o-semiquinone complexes on the nature of the substituent X can be used for the identification of the radical being attached.

Complexes 12–27 are stable in THF solutions in the absence of atmospheric oxygen and moisture for several days. The replacement of THF by other solvents causes symmetrization of lead mono-*o*-semiquinolates to form biradical complexes 5-7 (Scheme 4). The signals of starting complexes 12-27 in the isotropic ESR spectra disappear, and the anisotropic spectra show signals characteristic of compounds 5-7.

### Scheme 4



#### **Experimental**

All experiments associated with the synthesis and study of the properties of catecholate and o-semiquinolate lead(II) complexes were carried out under reduced pressure in the absence of traces of oxygen and water.

The solvents were purified and dried according to recommendations.<sup>33</sup> *o*-Quinones 2 <sup>34</sup>, 3 <sup>35</sup>, and 4 <sup>36</sup> and 3,6-di-*tert*butyl-2-ethoxyphenoxyl<sup>37</sup> were prepared according to known procedures. Copper, mercury, and silver halides, silver triflate, bezoyl peroxide, and iodine (Aldrich) were used without additional purification.

The IR spectra were measured on a Specord M-80 instrument in Nujol mulls. The ESR spectra were recorded on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT temperature controller. The *g* factors were measured with the use of diphenylpicrylhydrazyl as the standard (g = 2.0037). Synthesis of complexes 8–10 (general procedure). A solution of *o*-quinone 2 (1.10 g, 5.0 mmol) in THF (30 mL) was added with continuous stirring to an excess of lead metal (3.11 g, 15.0 mmol), after which the color of the reaction mixture changed from red-green through intense green-blue to yellow. Then the reaction mixture was separated from the unconsumed metal by decantation. After the addition of toluene or hexane to the resulting solution, a finely crystalline precipitate of complex 8 was obtained (2.05 g, 4.8 mmol) in 96.0% yield. Complex 8 is soluble in THF, dioxane, and dimethoxyethane, as well as in acetone on heating. Complex 8 is sensitive to atmospheric oxygen both in solution and the crystalline state.

Complexes 9 (91.9% yield) and 10 (89.3% yield) were prepared analogously starting from o-quinones 3 and 4, respectively.

Lead(II) 3,6-di-*tert*-butylcatecholate (8), yellow finely crystalline compound; decomposes without melting at a temperature higher than 260 °C. Found (%): C, 32.50; H, 3.98; Pb, 54.64.  $C_{14}H_{20}O_2$ Pb. Calculated (%): C, 32.76; H, 4.05; Pb, 54.74. IR, v/cm<sup>-1</sup>: 1245, 1150, 970, 920, 805, 730, 660.

**Lead(II) 3,6-di**-*tert*-butyl-4-methoxycatecholate (9), orange finely crystalline compound; decomposes without melting at a temperature higher than 315 °C. Found (%): C, 39.30; H, 4.67; Pb, 45.56.  $C_{15}H_{22}O_3$ Pb. Calculated (%): C, 39.38; H, 4.81; Pb, 45.29. IR, v/cm<sup>-1</sup>: 1235, 1100, 970, 870.

**Lead(II) 3,6-di**-*tert*-butyl-4-chlorocatecholate (10), orange finely crystalline compound; decomposes without melting at a temperature higher than 230 °C. Found (%): C, 36.50; H, 4.09; Pb, 44.30; Cl, 7.70.  $C_{14}H_{19}O_2PbCl$ . Calculated (%): C, 36.39; H, 4.12; Pb, 44.88; Cl, 7.68. IR, v/cm<sup>-1</sup>: 1290, 1235, 1155, 1055, 975, 945, 845.

Synthesis of complexes 5 and 6 (general procedure). Solutions of complex 8 (2.14 g, 5.0 mmol) and *o*-quinone 2 (1.1 g, 5.0 mmol) in THF (30 mL) were mixed in a 100-mL tube, after which the reaction mixture turned intense blue-green. The solvent was removed under reduced pressure, and the residue was dissolved in hot hexane. After cooling of the solution, needle-like crystals of complex 5 (3.00 g, 4.6 mmol, 92.8% yield) precipitated. Complex 5 is soluble in most of organic solvents. In the crystalline state, the complex is resistant to atmospheric oxygen. In solution, complex 5 slowly decomposes to form the corresponding o-quinone.

Complex 6 was prepared analogously starting from catecholate 9 and o-quinone 3 in 85.6% yield.

**Lead(II)** bis(3,6-di-*tert*-butyl-o-semiquinolate) (5), thin bluegreen needle-like crystals, m.p. 173 °C. Found (%): C, 51.83; H, 6.24; Pb, 32.01.  $C_{28}H_{40}O_4Pb$ . Calculated (%): C, 51.93; H, 6.18; Pb, 31.99. IR, v/cm<sup>-1</sup>: 1470, 1360, 1280, 1200, 950, 830.

**Lead(11)** bis(3,6-di-*tert*-butyl-4-methoxy-*o*-semiquinolate) (6), thin blue-green needle-like crystals, m.p. 153 °C. Found (%): C, 51.03; H, 6.41; Pb, 39.53.  $C_{30}H_{44}O_6Pb$ . Calculated (%): C, 50.92; H, 6.22; Pb, 39.28. IR, v/cm<sup>-1</sup>: 1460, 1395, 1325, 1250, 1190, 1100, 990, 880, 830.

Tetrakis(3,6-di-*tert*-butylcatecholato)-bis( $\mu_4$ -oxo)hexalead(II) hexakis(acetone) solvate (11). Complex 8 (1.28 g, 3.0 mmol) was refluxed in acetone (50 mL) containing water (0.5 mL) for 2 h until the compound was completely dissolved. Slow cooling afforded orange crystals of complex 11 (0.87 g, 0.35 mmol) in 70.3% yield.

Compound 11 is soluble in THF, dioxane, dimethoxyethane, acetone, and toluene on heating. At a temperature higher

than 40 °C, compound **11** loses acetone. At a temperature higher 150 °C, **11** decomposes without melting. Found (%): C, 35.24; H, 4.17; Pb, 49.86.  $C_{74}H_{116}O_{16}Pb_6$ . Calculated (%): C, 35.49; H, 4.64; Pb, 49.64. IR, v/cm<sup>-1</sup>: 1688, 1413, 1376, 1240, 1150, 966, 945, 931.

Synthesis of complexes 12–27 (general procedure). Equimolar amounts of complexes 8 (9 or 10) and different oxidizing agents (see Scheme 3) in THF were mixed in an ESR tube. Complexes 12–27 were studied in solution without isolation.

**X-ray diffraction study.** Single crystals of compound **11** were grown by slow cooling of an acetone solution. X-ray diffraction data were collected on a Smart Apex diffractometer (Mo-K $\alpha$ , graphite monochromator). The crystal dimensions are 0.25×0.20×0.10 mm. A total of 31929 reflections were measured, of which 7225 reflections ( $R_{int} = 0.0341$ ) were independent with  $I > 2\sigma(I)$ . The unit cell parameters for C<sub>37</sub>H<sub>58</sub>O<sub>8</sub>Pb<sub>3</sub> at 100(2) K: a = 15.7862(8) Å, b = 16.7512(9) Å, c = 15.9984(8) Å,  $\beta = 103.557^{\circ}$ , space group P2(1)/n, Z = 4, V = 4112.7(4) Å<sup>3</sup>,  $d_{calc} = 2.023$  g cm<sup>-3</sup>,  $\mu = 12.296$  mm<sup>-1</sup>,  $F(000) = 2360, 1.80^{\circ} \le 0 \le 25.00^{\circ}$ ,  $R_1 = 0.0210$  and  $wR_2 = 0.0485$  ( $I > 2\sigma(I)$ ),  $R_1 = 0.0248$  and  $wR_2 = 0.0495$  (based on all data)),  $S(F^2) = 1.129$ , the residual electron density (max/min) 0.919/-1.240 e Å<sup>-3</sup>.

The structure was solved by direct methods and refined by the full-matrix least-squares method against  $F^2$  with the use of the SHELXTL program package.<sup>38</sup> The semiempirical absorption correction was applied based on equivalent reflections using the SADABS program.<sup>39</sup> All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference electron density maps and refined isotropically, except for the H atoms of the solvent molecules.

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### References

- 1. J. Parr, Polyhedron, 1997, 16, 551.
- G. A. Abakumov, Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva, 1979, 156 [Mendeleev Chem. J., 1979 (Engl.Transl.)].
- V. I. Nevodchikov, G. A. Abakumov, V. K. Cherkasov, and G. A. Razuvaev, *J. Organomet. Chem.*, 1981, **214**, 119.
- 4. G. A. Abakumov, V. K. Cherkasov, K. G. Shalnova, I. A. Teplova, and G. A. Razuvaev, J. Organomet. Chem., 1982, 236, 333.
- G. A. Abakumov, A. V. Krashilina, V. K. Cherkasov, and L. N. Zakharov, *Dokl. Akad. Nauk*, 2003, **391**, 343 [*Dokl. Chem.*, 2003, **391**, 185 (Engl. Transl.)].
- K. A. Kozhanov, M. P. Bubnov, V. K. Cherkasov, G. K. Fukin, and G. A. Abakumov, *J. Chem. Soc. Dalton Trans.*, 2004, 2957.
- Z. K. Kasymbekova, A. I. Prokof ev, N. N. Bubnov, S. P. Solodovnikov, and M. I. Kabachnik, *Dokl. Akad. Nauk*

SSSR, 1982, 263, 352 [Dokl. Chem., 1982, 263 (Engl. Transl.)].

- G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, and N. O. Druzhkov, *Dokl. Akad. Nauk*, 2004, **399**, 353 [*Dokl. Chem.*, 2004, **399**, 223 (Engl. Transl.)].
- 9. G. A. Abakumov, V. I. Nevodchikov, V. K. Cherkasov, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1978, 242, 609 [*Dokl. Chem.*, 1978, 242 (Engl. Transl.)].
- S. V. Maslennikov, O. Y. Chekhonina, I. V. Spirina, A. V. Piskounov, and V. K. Cherkasov, *Main Group Metal. Chem.*, 2001, 24, 865.
- 11. G. M. Barnard, M. A. Brown, H. E. Mabrouk, B. A. McGarvey, and D. G. Tuck, *Inorg. Chim. Acta*, 2003, 349, 142.
- 12. C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
- 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.)].
- 14. J. Emsley, *The Elements*, Clarendon press, Oxford, 1991, 251 pp.
- G. A. Abakumov, V. A. Muraev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1974, **217**, 1083 [*Dokl. Chem.*, 1974, **217** (Engl. Transl.)].
- 16. E. S. Klimov, G. A. Abakumov, E. N. Gladyshev, P. Ya. Bayushkin, V. A. Muravev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1974, **218**, 844 [*Dokl. Chem.*, 1974, **218** (Engl. Transl.)].
- N. V. Berezina, V. K. Cherkasov, and V. P. Maslennikov, *Zh. Obshch. Khim.*, 1996, **66**, 1488 [*Russ. J. Gen Chem.*, 1996, **66**, 1451 (Engl. Transl.)].
- 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.)].
- 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.)].
- 20. N. V. Berezina, V. K. Cherkasov, A. V. Kondin, and V. P. Maslennikov, *Zh. Obshch. Khim.*, 1996, **66**, 40 [*Russ. J. Gen. Chem.*, 1996, **66**, 35 (Engl. Transl.)].
- 21. J. H. Sharp and M. C. R. Symons, in *Ions and Ion Pairs in Organic Reactions*, Wiley-interscience, New York, 1972, Vol. 1, p. 178.
- 22. A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance, with Applications to Chemistry and Chemical Physics*, Harper and Row, New York and London, 1967, 266 pp.

- 23. M. R. St J. Foreman, M. J. Plater, and J. M. S. Skakle, J. Chem. Soc. Dalton Trans., 2001, 1897.
- 24. C. Janiak, J. Chem. Soc. Dalton Trans., 2003, 2781.
- 25. W. Frank and F.-G. Wittmer, Chem. Ber., 1997, 130, 1731.
- 26. B. Tumanskii, P. Pine, Y. Apeloig, N. J. Hill, and R. West, J. Am. Chem. Soc., 2004, 126, 7786.
- I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, and M. P. Bubnov, *Inorg. Chem.*, 2004, 43, 7807.
- 28. 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.)].
- B. Tumanskii, P. Pine, Y. Apeloig, N. J. Hill, and R. West, J. Am. Chem. Soc., 2005, 127, 8248.
- A. V. Piskunov, I. A. Aivaz yan, V. K. Cherkasov, and G. A. Abakumov, J. Organomet. Chem., 2006, 691, 1531.
- P. Lihung, B. Twamley, and P. P. Power, *Organometallics*, 2000, **19**, 2874.
- 32. S. S. Al-Juaid, A. G. Avent, C. Eaborn, M. S. Hill, P. B. Hitchcock, D. J. Patel, and J. D. Smith, *Organometallics*, 2001, 20, 1223.
- 33. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley Interscience Publication, New York, 1972, 537 pp.
- 34. 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.)].
- 35. V. B. Vol'eva, I. A. Novikova, E. V. Ivanova, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1986, 215 [Bull. Acad. Sci. USSR. Div. Chem. Sci., 1986, 35 (Engl. Transl.)].
- 36. V. A. Garnov, V. I. Nevodchikov, G. A. Abakumov, V. K. Cherkasov, L. G. Abakumova, and Yu. A. Kurskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2793 [*Bull. Acad. Sci. USSR. Div. Chem. Sci.*, 1985, **34** (Engl. Transl.)].
- 37. G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, N. O. Druzhkov, G. K. Fukin, Y. A. Kursky, and A. V. Piskunov, *Tetrahedron Lett.*, 2005, **46**, 4095.
- G. M. Sheldrick, SHELXTL v. 6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.
- G. M. Sheldrick, SADABS v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.

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