b. Compound **4b** (0.3 g, 11.6 mmol) was added portionwise to the nitrating mixture prepared from HNO_3 (d = 1.5, 0.3 g) and Ac_2O (0.6 g) at 0 °C; the mixture was stirred at 5 °C for 1 h and poured into ice water. When the mixture was neutralized, the formed oil crystallized out. Compound **5b** was obtained in 80 % yield (0.4 g).

***N*-Trimethylsilyl-*O*-2,4-dinitrophenylhydroxylamine (4d).** All reactions with silyl-substituted compounds were carried out under argon in anhydrous CH_2Cl_2.

A solution of *N*-trimethylsilyl-*N,N'*-diphenylurea (0.84 g, 33.8 mmol) in 2 mL of CH_2Cl_2 was added to a suspension of **4c** (0.59 g, 29.6 mmol) in 1 mL of CH_2Cl_2 at 20 °C; the mixture was stirred for 20 min, the precipitate was filtered off and washed with CH_2Cl_2, then the solution was evaporated at 20 °C (10 Torr), and compound **4d** was obtained in 100 % yield (0.8 g). ^1H NMR (CH_2Cl_2, δ): 1.09 (s, MeSi). When **4d** was treated with methanol, compound **4c** was obtained in a quantitative yield.

1-Methoxy-2-(2,4-dinitrophenoxy)diazene 1-oxide (6). A solution of **4d** (2.17 g, 80 mmol) in 6 mL of CH_2Cl_2 was added to a suspension of $(NO_2)_2SiF_6$ (1 g, 40.3 mmol) in 2 mL of CH_2Cl_2 at −20 °C, and the mixture was stirred for 1 h at −15 to −10 °C. In the ^1H NMR spectrum of the reaction mixture, a doublet at δ 0.15 was observed (Me_3SiF). When volatile compounds were distilled off at −15 to −10 °C (8 Torr), an ether solution of diazomethane (170 mmol) was added dropwise to the residue, the mixture was stirred at −10 to −5 °C for 20 min, then ether was distilled off at 20 °C, and compound **6** (0.64 g, 31 %), m.p. 95—96 °C (EtOH), was obtained by preparative TLC of the residue (silica gel 5/40, a 6 : 1 benzene—chloroform mixture was used as the eluent), R_f = 0.6. Found (%): C, 32.61; H, 2.31; N, 21.34. $C_7H_6N_4O_7$. Calculated (%): C, 32.54; H, 2.31; N, 21.69. ^1H NMR ($CDCl_3$, δ): 4.06 (predominant isomer); 4.09 (minor isomer) (s, 3 H, Me). ^{13}C NMR (DMSO-d_6): predominant isomer: 58.9 (Me), 118.8, 122.5, 130.7, 137.6, 143.3, 153.0 (C arom.); minor isomer: 58.4 (Me), 118.5, 122.5, 130.7, 137.4, 143.1, 153.8 (C arom.).

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Complexes of lanthanum with radical anions of 2,2-bipyridyl and 3,6-di-*tert*-butyl-*o*-benzoquinone

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Complexes of a rare-earth element containing only one radical-anion ligand have been synthesized and isolated in pure states for the first time. The $LaI_2(bpy)(THF)_3$ complex has been prepared from $[LaI_2(THF)_3]_2(C_{10}H_8)$ and 2,2-bipyridyl in DME. The semiquinone complex $LaI_2(SQ)(THF)_3$ has been obtained by reaction of lanthanum iodide with 3,6-di-*tert*-butyl-*o*-benzoquinone in THF in the presence of lanthanum powder. ESR spectra of the complexes have been studied.

Key word: lanthanum, radical-anion ligands, ESR spectra.

Various complexes of most transition and non-transition metals with radical-anion ligands have been synthesized and studied by ESR spectroscopy. Nevertheless, only a few complexes of such kind are known in

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the group of rare-earth elements. We have synthesized the first complexes of lanthanum(III) with the only one radical-anion ligand, *i.e.*, $LaI_2(bpy)^{-}(bpy)(DME)_2$ (**1**) (bpy = 2,2-bipyridyl) and $LaI_2(SQ)(THF)_3$ (**2**) (SQ = 3,6-di-*tert*-butyl-*o*-benzosemiquinone).

Complex **1** has been prepared by the reaction of the known binuclear complex $[LaI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$[1] containing bridging naphthalene dianion with 2,2-bipyridyl in 1,2-dimethoxyethane (DME).

$$[LaI_2(THF)_3]_2(C_{10}H_8) + 4bpy \xrightarrow{DME} \underset{\mathbf{1}}{2LaI_2(bpy)^{-\cdot}(bpy)(DME)_2} + C_{10}H_8$$

Compound **1** has been obtained as dark-red crystals, poor soluble in THF and insoluble in DME; **1** is decomposed under heating above 160 °C. ESR spectrum of the complex in THF exhibits hyper-fine structure which is caused by the coupling of unpaired electron with ^{14}N and ^{1}H nuclei of bpy-ligand and ^{139}La nucleus (hyper-fine splitting constants $a_N = 1.3$ Oe (4×N), $a_H = 0.26$ Oe (2×H), $a_H = 0.13$ Oe (4×H), $a_H \approx 0.03$ Oe (2×H), and $a_{La} = 0.59$ Oe). IR spectrum of **1** consists of absorption bands of bpy ligand and coordinated DME molecules. The effective magnetic moment of $LaI_2(bpy)(DME)_3$ (1.6 mB at 293 K) is close to the theoretical one for one unpaired electron localized on a ligand. When vanadocen was added to the solution of **1** in THF the initial ESR signal disappeared and a signal of tris(2,2-bipyridyl)vanadium(0) ($a_V = 83.5$ Oe)[2] was observed.

Complex **2** has been obtained in reaction of lanthanum(III) iodide with 3,6-di-*tert*-butyl-*o*-benzoquinone (Q) in THF in the presence of a stoichiometric amount of lanthanum metal.

$$2LaI_3(THF)_3 + 3Q + La \xrightarrow{THF} \underset{\mathbf{2}}{3LaI_2(SQ)(THF)_3}$$

Compound **2** is dark crystals, easily soluble in THF and benzene and slightly soluble in diethyl ether. The ESR spectrum of **2** in THF exhibits hyper-fine structure due to the interaction of unpaired electron with two protons of semiquinone ligand and ^{139}La nucleus: $a_H \cong a_{La} \cong 3.6$ Oe, g = 2.0030. ESR spectrum of crystalline **2** is broadened singlet, $g = 2.0050$. In the case of THF/H_2O solution ESR spectrum exhibits as well resolved multiplet with narrow lines, $a_H = 3.8$ Oe и $a_{La} = 3.2$ Oe. The IR spectrum of **2** consists of the absorption band at 1500 cm^{-1} (νC—O), which indicates the presence of SQ-ligand. The frequency of the last one is the same as for SQ complexes of sodium or zinc.

Effective magnetic moment of complex **2** (1.2 mB at 293 K) is essentially smaller than expected value for one electron localized on SQ ligand. Our experimental data do not allow an explanation of such a lowered value of the magnetic moment.

An X-ray crystal structure analysis of the complexes described above is in progress.

Experimental

The above-mentioned synthesis and all manipulation of prepared compounds were conducted in a vacuum with rigorous exclusion of air and moisture using standard Schlenk techniques. Tetrahydrofuran and 1,2-dimethoxyethane were condensed from sodium ketyl. The complex $[LaI_2(THF)_3]_2(C_{10}H_8)$ was prepared by stirring equimolar quantities of $LaI_3(THF)_3$ and lithium with excess naphthalene in THF. $LaI_3(THF)_3$ was obtained from lanthanum metal and CH_2I_2 in THF. Recrystallization from THF gives $LaI_3(THF)_3$ as colorless crystals. IR spectra were recorded for Nujol suspensions with a Specord-M80 spectrometer. ESR spectra were registered using a Bruker ER 200D-SCR spectrometer (9350 MHz).

Synthesis of $LaI_2(bpy)(DME)_3$ (1). A solution of 2,2-bipyridyl (0.4 g, 2.56 mmol) in DME (20 mL) was added to a suspension of $[LaI_2(THF)_3]_2(C_{10}H_8)$ (1.55 g, 1.15 mmol) in DME (25 mL) with vigorous stirring. The powder of the complex $[LaI_2(THF)_3]_2(C_{10}H_8)$ gradually dissolved, and a brown-red solution formed. After 5—10 min dark crystals precipitated from the solution. After 2 h of storage the solution was decanted, and the resulting crystalline product was washed with cold DME (2×10 mL) and dried in vacuum, yielding 0.8 g (80 %) of dark-red, almost black crystals of **1**, which decomposed above 160 °C. Found (%): La, 15.8. $C_{22}H_{38}O_6N_2I_2La$. Calculated (%): La, 16.4. IR, ν/cm^{-1}: 1595, 1570, 1548, 1505, 1420, 1320, 1296, 1280, 1260, 1225, 1190, 1150, 1120, 1085, 1030, 1020, 1010, 945, 840, 765, 735, 685, 645, 625, 610, 450, 420. Magnetic susceptibility: $\chi^{293} = 1080 \times 10^{-1}$ sgsu, $\mu_{eff} = 1.6$ mB.

Synthesis of $LaI_2(SQ)(THF)_3$ (2). A mixture of lanthanum filings (0.37 g, 2.66 mg-atom), $LaI_3(THF)_3$ (4.1 g, 5.57 mmol) and 3,6-di-*tert*-butyl-*o*-benzoquinone (1.8 g, 8.18 mmol) was stirred in THF (35 mL) at room temperature. After 16 h lanthanum metal and lanthanum iodide completely dissolved to give a green-brown solution. The solvent was removed in a vacuum and benzene was added to the residual oil. Then benzene was removed and waxy residue was dissolved with 50 mL of diethyl ether. During keeping this solution for 28 h at −10 °C dark crystals were precipitated. Yield: 3.1 g (45 %) of **2**, which decomposed above >150 °C. Found (%): La, 16.7. $C_{28}H_{44}O_5I_2La$. Calculated (%): La, 16.3. IR, ν/cm^{-1}: 1500, 1390, 1370, 1350, 1320, 1285, 1210, 1180, 1150, 1130, 1030, 960, 950, 920, 870, 850, 810, 675, 660, 530, 500, 470, 440. Magnetic susceptibility: $\chi_{293} = 609 \times 10^{-1}$ sgsu, $\mu_{eff} = 1.2$ mB.

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