



## Synthesis and characterization of phenanthren-*o*-iminoquinone complexes of rare earth metals

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### ARTICLE INFO

#### Article history:

Received 22 April 2010

Received in revised form

11 June 2010

Accepted 25 June 2010

Available online 3 July 2010

Dedicated to the memory of Professor Herbert Schumann with whom many years of close friendship and fruitful collaboration bonded us.

#### Keywords:

Phenanthren-*o*-iminoquinone

Scandium

Neodymium

Dysprosium

Ytterbium

### ABSTRACT

The complexes  $\text{Ln}(\text{L})_3$  ( $\text{L} = \text{N}$ -(2,6-di-isopropylphenyl)-phenanthren-*o*-iminoquinone,  $\text{Ln} = \text{Sc}$  (**1**),  $\text{Yb}$  (**2**)) were synthesized by the reactions of phenanthren-*o*-iminoquinone **L** with scandium or ytterbium metals in benzene medium. The X-ray analysis revealed that the molecule of **2** consists of  $\text{Yb}^{3+}$  cation coordinated by three phenanthren-*o*-iminoquinone ligands in  $\eta^2$  fashion. Both complexes are paramagnetic. The magnetic moments of **1** ( $2.7 \mu_{\text{B}}$ ) are consistent with the formulation  $\text{Sc}(\text{L}^-)_3$  ( $\text{L}^- =$  radical anion), in which spins on the individual units are uncoupled. The magnetic moments of **2** ( $3.7 \mu_{\text{B}}$ ) indicate some antiferromagnetic coupling of paramagnetic centers in the molecules. The EPR spectrum of **1** in toluene exhibits a broad unresolved signal with  $g$  2.0029 assigned to unpaired electrons of phenanthren-*o*-iminoquinone ligands. The reactions of phenanthren-*o*-iminoquinone **L** with  $\text{NdI}_2$  and  $\text{DyI}_2$  in benzene led to formation of iodide/phenanthren-*o*-iminoquinone complexes  $\text{I}_2\text{Ln}(\text{L})_2$  of  $\text{Nd}(\text{III})$  (**3**) and  $\text{Dy}(\text{III})$  (**4**). Besides, from the reaction with  $\text{DyI}_2$  the product of partial disproportionation of **4** was isolated and identified as homoleptic complexes  $\text{Dy}(\text{L})_3$  (**5**), structure of which turned out identical to that of **2**. The same reactions in ether or crystallization of **3** and **4** from ether yielded solvated complexes  $\text{I}_2\text{Ln}(\text{L})_2(\text{Et}_2\text{O})_2$  ( $\text{Ln} = \text{Nd}$  (**6**),  $\text{Dy}$  (**7**)). The X-ray analysis of **6** and **7** has displayed unprecedented for iminoquinonates  $\eta^1$  mode of metal–ligand coordination. Magnetic moments of **3**, **4**, **6** and **7** ( $3.3$ ,  $10.4$ ,  $3.4$  and  $10.6 \mu_{\text{B}}$  respectively) corresponding to  $\mu_{\text{eff}}$  of  $\text{Nd}(\text{III})$  and  $\text{Dy}(\text{III})$  suggest that in the compounds exists quick reversible intramolecular interligand electron transfer which results in diamagnetism of the total ligand system. Magnetic moment of **5** ( $12.8 \mu_{\text{B}}$ ) corresponds to formulation of  $\text{Dy}^{3+}(\text{L}^-)_3$  with uncoupled spins of metal atom and the ligands.

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### 1. Introduction

It is well known that *o*-quinones in the complexes with transition and nontransition metals can exist as neutral, radical anion (*o*-semiquinone) or dianion (catecholate) ligands [1–3]. Unusual ability of such compounds to intramolecular redox transformations (valence tautomerism) and presence in the semi-quinolates unpaired electrons, which allow using EPR spectroscopy and magnetic measurements for their study, make these derivatives unique objects for investigation of the nature of metal–ligand interaction [4–6]. The complexes with *o*-iminoquinones, which are closest electron analogues of *o*-quinones, are studied in essentially less extent although these ligands also are able to serve as neutral, radical anion (iminosemiquinolates) or dianion (amidophenolates)

*O,N*-chelate ligands. Comprehensive review devoted to 4,6-di-*tert*-butyl-*N*-aryl(alkyl)-*o*-iminobenzoquinonato complexes of transition metals has been published recently [7]. In this review and some original papers one can find the description of homoleptic and heteroleptic iminobenzoquinolates of Zr, V, Cr, Mn [8], Re [9], Fe, Ru [10], Os, Co, Ir, Ni, Pd, Pt, Cu, Ga, Tl, Ge and Sn. Phenanthren-*o*-iminoquinone complex is known for Ni [11]. Oxidation states of metal and ligand in these compounds depend on ionization potential of the metal and the nature of ancillary ligands (in heteroleptic complexes). As far as we know, a sole example of rare earth metal iminoquinolates is the complexes of  $\text{Sc}(\text{OTf})_3(\text{TTQ})$  where TTQ (tryptophan tryptophylquinone derivatives) are cofactor of quinoprotein methylamine and aromatic amine [12]. The complexes have not been isolated from reaction mixtures but were identified by spectroscopy and used *in situ* as catalysts for oxidation of benzylamine to *N*-benzylidenebenzylamine. At the same time, the *o*-iminoquinolate complexes of 3 group metals and especially their phenanthren-*o*-iminoquinone analogues, which is

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known so far only for Ni [11], are of special interest not only as unique objects for academic investigation but as well as potential materials for optoelectronic devices. Similarity of N,O-Ln chelate fragments and conjugated  $\pi$ -electron system in the phenanthren-*o*-iminoquinolates to those in the known lanthanide based electroluminophores [13] gives the ground to expect from these compounds effective luminescent properties. Herein, we describe the synthesis and characterisation of the first *o*-iminophenolate complexes of scandium and some lanthanides. The homoleptic compounds of Ln(L)<sub>3</sub> were prepared for Sc(III) and Yb(III) by direct reactions of the metals with quinone L. The diiodide/phenanthren-*o*-iminoquinonates I<sub>2</sub>Ln(L)<sub>2</sub> of Nd(III) and Dy(III) were synthesized by the reactions of LnI<sub>2</sub> with L. Luminescent properties of the obtained compounds turned out very weak but quite unusual for quinonates and iminoquinonates arrangement of Nd and Dy derivatives has justified the efforts spent for this study.

## 2. Experimental section

### 2.1. General methods

The syntheses and manipulations of the extremely air and moisture sensitive compounds described below were conducted with rigorous exclusion of air and water using Schlenk techniques. Reagent-grade chemicals were used in all experiments, and solvents were purified using standard procedures. Sc metal and Y metal were purchased from Aldrich. At a final stage of purification THF and ether were treated with NdI<sub>2</sub> for 10 min before use and collected in a reaction vessel by condensation in vacuum. N-(2,6-Di-isopropylphenyl)-phenanthren-*o*-iminoquinone [11] and the diiodides LnI<sub>2</sub> (Ln = Nd, Dy) were prepared using procedures described previously [14]. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with Euro EA 3000 Elemental Analyser.

Content of metal was determined by complexometric titration after preliminary oxidation of the samples in air and removal of the split organic ligands.

### 2.2. Physical measurements

IR spectra were recorded on a Specord M-75 spectrometer and recorded from 4000 to 450 cm<sup>-1</sup>. The samples were prepared as Nujol mulls and as films between KBr plates. <sup>1</sup>H NMR spectra were recorded on Bruker DPX 200 and Bruker Avance III NMR spectrometers, operating at 200 and 400 MHz, respectively. UV–vis spectra were recorded with a Perkin–Elmer Lambda 25 spectrometer in a region from 380 to 1100 nm. The photoluminescence spectra were recorded from 400 to 800 nm on a spectrometer Fluorescence LS-55 (spectral resolution 1 nm) with excitation at 300–400 nm. EPR spectra were recorded on Bruker EMX spectrometer, operating in X-band and equipped by ER 4105 DR cavity (work frequency 9.75 GHz) and equipped with ER 4111 VT temperature controller. *g*-Factors values were determined using DPPH (*g* = 2.0037) as a standard. Magnetic moments were measured by Faraday method at room temperature as described previously [15].

### 2.3. Preparation of Sc(C<sub>26</sub>H<sub>25</sub>NO)<sub>3</sub> (1)

A mixture of thin shavings of scandium metal (0.7 g, 7.17 mmol), phenanthren-*o*-iminoquinone L (0.2 g, 0.544 mmol), iodine (15 mg, 0.006 mmol) in benzene (7 ml) was stirred for 10 h at 50 °C. During this time, initial blue color of the solution turned dark brown. The reaction solution was separated from excess of metal by decantation and cooled to room temperature to give the first crop of 1

(91 mg) as black crystals. The second portion of the product (48 mg) has precipitated after concentration of a solution to 3 ml. Total yield of **1** was 0.139 g (67%), m.p. > 210 °C (dec.),  $\mu_{\text{eff}}$  2.7  $\mu_{\text{B}}$ . Anal. Calcd for C<sub>78</sub>H<sub>75</sub>N<sub>3</sub>O<sub>3</sub>Sc (1147.40): C, 81.65; H, 6.59; N, 3.66. Found: C, 81.01; H, 6.68; N, 3.43%. IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 3070 w, 1597 m, 1574 m, 1500 m, 1480 s, 1424 s, 1315 m, 1244 m, 1127 m, 1080 m, 1040 m, 949 m, 789 s, 758 s, 719 s, 679 s. <sup>1</sup>H NMR (THF-d<sub>8</sub>,  $\delta$  ppm, 400 MHz): broad peaks in area 0–12 ppm with maxima at 1.3, 3.2, 5.1, 9.5, 10.7 and 11.9. Signals of the complex are superimposed with the signals of free phenanthren-*o*-iminoquinone (*J*, Hz): 1.02 and 1.11 (both d, both 6H, *J* = 6.8, CH<sub>3</sub>); 2.66 (septet, 2H, *J* = 6.8, CHMe<sub>2</sub>); 6.98 (t, 1H, *J* = 7.6); 7.09 (d, 2H, *J* = 7.7); 7.42 (t, 1H, *J* = 7.5); 7.50 (t, 1H, *J* = 7.2); 7.64 (t, 1H, *J* = 7.6); 7.72 (t, 1H, *J* = 7.7); 7.91 (d, 1H, *J* = 8.2); 8.21 (m, 2H); 8.37 (d, 1H, *J* = 8.2).

### 2.4. Preparation of Yb(C<sub>26</sub>H<sub>25</sub>NO)<sub>3</sub> (2)

To a mixture of ytterbium shavings (1.24 g, 7.17 mmol), phenanthren-*o*-iminoquinone L (0.2 g, 0.544 mmol) and iodine (15 mg, 0.006 mmol) 7 ml THF were added. The mixture was stirred for 10 h at ambient temperature. Color of a solution gradually changed from dark blue to dark brown. Solution was decanted from excess of shavings, THF was removed in vacuum and ether (7 ml) was added to the rest. Obtained solution was filtered, concentrated to 3 ml and cooled at 0 °C to give 159 mg (69%) of **2** as black crystals with m.p. 233 °C (dec.);  $\mu_{\text{eff}}$  3.7  $\mu_{\text{B}}$ . The compound isolates with one molecule of crystallizing ether. One of the crystals was used for X-ray analysis. Anal. Calcd for C<sub>82</sub>H<sub>85</sub>N<sub>3</sub>O<sub>4</sub>Yb (1349.61): C, 72.97; H, 6.35; N, 3.11. Found: C, 73.38; H, 5.93; N, 3.02%. IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 3070 w, 1685 m, 1594 m, 1581 m, 1282 m, 1249 m, 1160 m, 1098 m, 1040 m, 786 m, 758 s, 721 s, 680 s. <sup>1</sup>H NMR (THF-d<sub>8</sub>,  $\delta$  ppm, 400 MHz): broad peaks at –22.9, –11.3, –9.9, –4.2 and –2.6. Signals of the complex are superimposed partially with widened peaks of free phenanthren-*o*-iminoquinone.

### 2.5. Reaction of NdI<sub>2</sub> with phenanthren-*o*-iminoquinone L

A mixture of NdI<sub>2</sub> (317 mg, 0.796 mmol), phenanthren-*o*-iminoquinone L (585 mg, 1.59 mmol) and 10 ml of benzene was stirred for 8 h at 50 °C. After cooling to room temperature 40 ml of benzene was added to the reaction solution. Obtained mixture was filtered and a solid residue was extracted twice by benzene. The filtrate and the extracts were joined and solvent was removed by vacuum evaporation. The remained black–brown crystalline solid was washed with hexane and dried in vacuum to give 590 mg (65%) of **3**; m.p. > 120 °C (dec.);  $\mu_{\text{eff}}$  3.3  $\mu_{\text{B}}$ . Anal. Calcd for C<sub>52</sub>H<sub>50</sub>I<sub>2</sub>N<sub>2</sub>NdO<sub>2</sub> (1133.01): C, 55.12; H, 4.45; N, 2.47. Found: C, 55.90; H, 4.87; N, 2.13%. IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 3070 w, 1685 m, 1594 m, 1581 m, 1282 m, 1249 m, 1160 m, 1098 m, 1040 m, 786 m, 758 s, 721 s. <sup>1</sup>H NMR (benzene-d<sub>6</sub>,  $\delta$  ppm, 400 MHz): broad singlets at –138.2; –117.6; –111.0; –6.5; 0.9 and 1.2 (12H, CH<sub>3</sub>); 4.3 (2H, CHMe<sub>2</sub>); 24.8 (2H); 34.1; 37.5; 41.3; 44.4; 46.6 (2H). <sup>1</sup>H NMR (THF-d<sub>8</sub>,  $\delta$  ppm, 400 MHz): broad singlets at –3.2; 4.6; 13.8; 17.9 and 31.1; the signals of free phenanthren-*o*-iminoquinone (*J*, Hz): 1.02 and 1.11 (both d, both 6H, *J* = 6.8, CH<sub>3</sub>); 2.66 (septet, 2H, *J* = 6.8, CHMe<sub>2</sub>); 6.98 (t, 1H, *J* = 7.6); 7.09 (d, 2H, *J* = 7.7); 7.42 (t, 1H, *J* = 7.5); 7.50 (t, 1H, *J* = 7.2); 7.64 (t, 1H, *J* = 7.6); 7.72 (t, 1H, *J* = 7.7); 7.91 (d, 1H, *J* = 8.2); 8.21 (m, 2H); 8.37 (d, 1H, *J* = 8.2).

### 2.6. Reaction of DyI<sub>2</sub> with phenanthren-*o*-iminoquinone L

To DyI<sub>2</sub> (329 mg, 0.79 mmol) was added phenanthren-*o*-iminoquinone L (581 mg, 1.58 mmol) in 13 ml of benzene. After stirring during 10 h at 50 °C the reaction solution was separated from precipitate by decantation, solvent was removed in vacuum and

10 ml of hexane was added to a residue. The formed brown solution was concentrated to 5 ml and left at 0 °C for 8 h. Deposited dark brown crystals of **5** were separated by decantation, washed by cold hexane and dried in vacuum. Yield 70 mg (14%);  $\mu_{\text{eff}}$  12.8  $\mu_{\text{B}}$ . One of the crystals was used for X-ray analysis. Anal. Calcd for  $\text{C}_{78}\text{H}_{75}\text{DyN}_3\text{O}_3$  (1264.95): C, 74.06; H, 5.98; N, 3.32. Found: C, 74.03; H, 6.02; N, 3.10%. IR spectrum of **5** is identical to that of **2**.

To a residue remained after separation of reaction solution benzene (40 ml) was added. The solution was filtered, benzene was removed and a residue was washed with hexane to give (215 mg, 24%) of **4**;  $\mu_{\text{eff}}$  10.4  $\mu_{\text{B}}$ . Anal. Calcd for  $\text{C}_{52}\text{H}_{50}\text{DyI}_2\text{N}_2\text{O}_2$  (1151.27): C, 54.25; H, 4.38; N, 2.43. Found: C, 53.87; H, 4.56; N, 2.13%. IR spectrum coincides with that of **3**.

### 2.7. Synthesis of $\text{NdI}_2(\text{C}_{26}\text{H}_{25}\text{NO})_2(\text{Et}_2\text{O})_2$ (**6**)

Phenanthren-*o*-iminoquinone L (260 mg, 0.708 mmol) in 7 ml of ether was added to  $\text{NdI}_2$  (141 mg, 0.35 mmol), the mixture was stirred for 4 h at room temperature and left for a night. The formed black crystals were separated by decantation and washed with cold ether to give 160 mg (45%) of complex **6**; m.p. > 215 °C (dec.);  $\mu_{\text{eff}}$  3.4  $\mu_{\text{B}}$

Anal. Calcd for  $\text{C}_{60}\text{H}_{70}\text{I}_2\text{N}_2\text{NdO}_4$  (1281.26): C, 56.24; H, 5.51; N, 2.19. Found: C, 55.44; H, 5.77; N, 2.13%. IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 3120 m, 3064 w, 1578 m, 1576 m, 1350 m, 1249 m, 1204 m, 1166 m, 1121 m, 1035 m, 923 m, 794 m, 758 s, 722 s, 677 s.

### 2.8. Synthesis of $\text{DyI}_2(\text{C}_{26}\text{H}_{25}\text{NO})_2(\text{Et}_2\text{O})_2$ (**7**)

Phenanthren-*o*-iminoquinone L (295 mg, 0.80 mmol) and ether (7 ml) were added to powder of  $\text{DyI}_2$  (167 mg, 0.40 mmol) and the mixture was stirred for 1 h at ambient temperature. The formed brown solution and brown precipitate were separated by decantation; ether was condensed back to precipitate and decanted again. The procedure was repeated four times. During this procedure black crystals of **7** were formed in the solution. The crystals were separated by decantation, washed with cold ether and dried in vacuum. Yield 0.173 g (33%); m.p. 234 °C (dec.);  $\mu_{\text{eff}}$  10.6  $\mu_{\text{B}}$ . One of the crystals was used for X-ray analysis.

Anal. Calcd for  $\text{C}_{60}\text{H}_{70}\text{DyI}_2\text{N}_2\text{O}_4$  (1299.52): C, 55.45; H, 5.43; N, 2.16. Found: C, 54.87; H, 5.77; N, 1.89%. IR (Nujol,  $\nu/\text{cm}^{-1}$ ): 3297 (m), 3147 (m), 3072 (w), 1574 (m), 1561 (m), 1528 (m), 1500 (s), 1351 (s), 1216 (m), 1120 (m), 1036 (m), 930 (m), 761 (s), 721 (s), 676 (m), 634 (m).

### 2.9. X-ray crystallography

The X-ray diffraction data were collected on a SMART APEX diffractometer (graphite-monochromated,  $\text{MoK}_\alpha$ -radiation,  $\phi$ - $\omega$ -scan technique,  $\lambda = 0.71073$  Å). The intensity data were integrated by SAINT program [16]. SADABS [17] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on  $F^2$  using all reflections with SHELXTL package [18]. All non-hydrogen atoms were refined anisotropically. The H atoms in all complexes were placed in calculated positions and refined in the "riding-model" ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  in  $\text{CH}_3$ -groups и  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  in other ligands). It was found a solvate  $\text{Et}_2\text{O}$  molecule in **2**. The details of crystallographic, collection and refinement data for **2**, **5**, **6** and **7** are shown in Table 1. CCDC-770753 (**2**), 770754 (**5**), 770755 (**6**), 770756 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; Email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

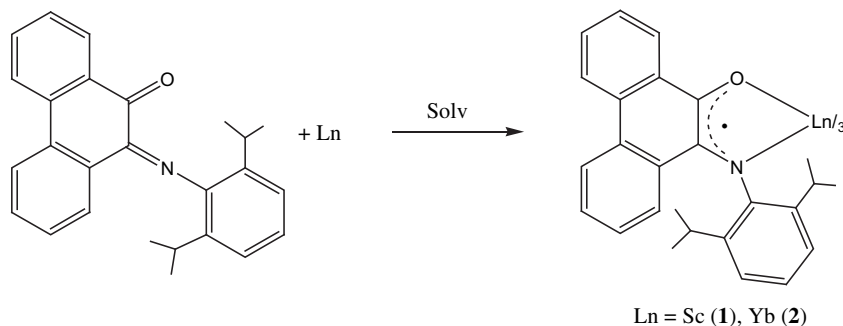
## 3. Results and discussion

### 3.1. Synthesis and characterization of homoleptic $\text{Ln}(\text{L})_3$ complexes of $\text{Sc}(\text{III})$ and $\text{Yb}(\text{III})$

It was found that treatment of Sc or Yb shavings activated by iodine with diluted solution of N-(2,6-di-isopropylphenyl)-phenanthren-*o*-iminoquinone in benzene affords phenanthren-*o*-iminoquinolates  $\text{Ln}(\text{L})_3$  in yields of up to 69%. The reactions transformations are easily traced by color change of the solutions from dark green to brown. In THF or ether solutions the reactions proceed faster but are accompanied by side processes which decrease the products yields.

**Table 1**  
The details of crystallographic, collection and refinement data for **2**, **5**, **6** and **7**.

	<b>2</b>	<b>5</b>	<b>6</b>	<b>7</b>
Empirical formula	$\text{C}_{82}\text{H}_{85}\text{N}_3\text{O}_4\text{Yb}$	$\text{C}_{78}\text{H}_{75}\text{DyN}_3\text{O}_3$	$\text{C}_{60}\text{H}_{70}\text{I}_2\text{N}_2\text{NdO}_4$	$\text{C}_{60}\text{H}_{70}\text{DyI}_2\text{N}_2\text{O}_4$
Formula weight	1349.57	1264.91	1281.22	1299.48
Crystal system	Hexagonal	Monoclinic	Triclinic	Triclinic
Space group	$P6(5)$	$P2(1)/n$	P-1	P-1
Unit cell dimensions				
<i>a</i> [Å]	13.3251(3)	18.956(3)	8.5934(15)	8.6160(9)
<i>b</i> [Å]	13.3251(3)	17.086(2)	9.6360(17)	9.6646(10)
<i>c</i> [Å]	68.037(3)	19.215(3)	17.823(3)	17.6734(18)
$\alpha$ [°]	90	90	98.166(4)	98.275(2)
$\beta$ [°]	90	91.077(3)	103.272(4)	103.418(2)
$\gamma$ [°]	90	90	100.688(4)	101.085(2)
Volume [Å <sup>3</sup> ]	10,462.0(5)	6222.2(15)	1385.0(4)	1377.1(2)
Z	6	4	1	1
Density (calculated) [g cm <sup>-3</sup> ]	1.285	1.350	1.536	1.567
Absorption coefficient [mm <sup>-1</sup> ]	1.393	1.254	2.098	2.524
$\theta$ range for data collection [°]	25.00	26.00	26.00	27.50
Reflections collected/unique	82,573/12,231	34,777/12,211	7728/5203	13,028/6261
<i>R</i> (int)	0.1328	0.0513	0.0378	0.0369
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.1174 w <i>R</i> 2 = 0.2399	<i>R</i> 1 = 0.0351 w <i>R</i> 2 = 0.0728	<i>R</i> 1 = 0.0907 w <i>R</i> 2 = 0.2174	<i>R</i> 1 = 0.0636 w <i>R</i> 2 = 0.1581
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1244 w <i>R</i> 2 = 0.2429	<i>R</i> 1 = 0.0816 w <i>R</i> 2 = 0.0834	<i>R</i> 1 = 0.1514 w <i>R</i> 2 = 0.2465	<i>R</i> 1 = 0.1045 w <i>R</i> 2 = 0.1780
Goodness-of-fit on $F^2$	1.155	0.912	1.076	1.031
Largest diff. peak and hole [e/Å <sup>3</sup> ]	1.812/−4.736	1.295/−1.053	2.033/−2.168	1.939/−2.089



The complexes **1** and **2** were isolated as air sensitive dark brown crystalline solids readily soluble in THF, sparingly – in ether and toluene but feeble soluble in hexane. Both complexes were identified by elemental analysis, IR and  $^1\text{H}$  NMR spectroscopy. Similar complex of dysprosium (**5**) has been isolated from the reaction of phenanthren-*o*-iminoquinone L with  $\text{DyI}_2$  (vide infra).

Structures of **2** and **5** were established by X-ray diffraction study which revealed that molecules of the complexes consist of  $\text{Ln}^{3+}$  cation coordinated by three equal phenanthren-*o*-iminosemiquinonate ligands (Fig. 1, Table 2).

Close values of Yb–O (2.155(8)–2.177(7) Å), Yb–N (2.348(9)–2.402(7) Å), O–C (1.284(12)–1.320(17) Å) and N–C (1.354(14)–1.375(11) Å) bond lengths indicate that all three ligands are bearing the same charge and do not differ from each other on character of interaction with Yb atom. Magnitudes of O–C, C–C and C–N distances as well as valent angles in the Yb–OCCN-chelate groups coinciding with the values of corresponding bonds and angles in molecules of 4,6-di-*tert*-butyl-N-(2,6-di-isopropylphenyl)-*o*-iminobenzosemiquinonate complexes of Mn(II) and Re(II), for which free-radical nature of the ligands and delocalization of a charge in the –OCCN– groups were strictly documented [8,9], suggest analogue type of metal–ligand interaction

in compound **2**. The same molecular arrangement has been established in **5**.

Both complexes **1** and **2** are paramagnetic. Effective magnetic moment of **1** ( $2.7 \mu\text{B}$ ) is consistent with the formulation  $\text{Sc}^{3+}(\text{L}^{\cdot-})_3$  ( $\text{L}^{\cdot-}$  = radical anion), in which spins on the individual units are uncoupled. Magnetic moment of **2** ( $3.7 \mu\text{B}$ ) is less than expected (ca.  $7 \mu\text{B}$ ) for the four uncoupled spin carriers,  $\text{Yb}^{3+}(4f^{13})$  and three phenanthren-*o*-iminoquinone radical anions, which implies exchange coupling between the spins. Similar coupling was observed previously for the complexes of  $\text{Yb}^{3+}$  with diazabutadiene, 4,4'-bipyridine and some other N,N-chelating ligands [19].

The EPR spectrum of crystalline **1** and its solution in toluene registered at 290 K represents a broad unresolved singlet with  $g = 2.0029$ . The anisotropic spectrum in toluene matrix at 150 K shows superposition of a singlet and a set of signals characteristic for three radical units with the split parameters in zero field  $D = 181 \text{ mT}$ ,  $E = 4.3 \text{ mT}$ . Besides, a signal corresponding to transition of  $\Delta m_s = 2$  is observed in a half-field. Neither crystalline nor solutions of **2** display EPR signals at room temperature and 150 K apparently because of above mentioned antiferromagnetic coupling.

The  $^1\text{H}$  NMR spectra of **1** and **2** in THF- $\text{D}_8$  are identical and contain two sets of signals. Signals of the first group (1.02–2.66, 6.98–8.37 ppm) are sharp and their positions exactly correspond to the spectra of free phenanthren-*o*-iminoquinone L. Signals of the second set, which assigned to the protons of charged phenanthren-*o*-iminoquinone ligands (0–12 (Sc), –23 to 2 (Yb) ppm), are broadened and shifted (in the case of Yb) to high field that is characteristic for paramagnetic compounds. These data suggest that in THF solutions **1** and **2** exist in equilibrium with their amidophenolate form.

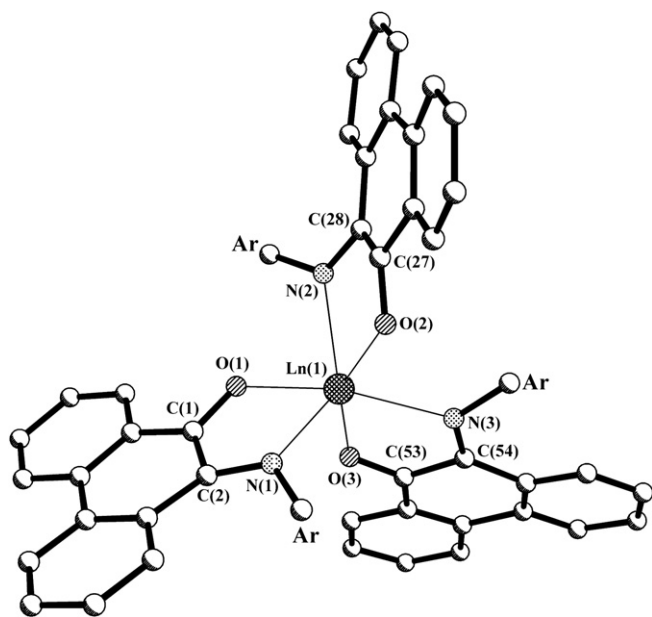
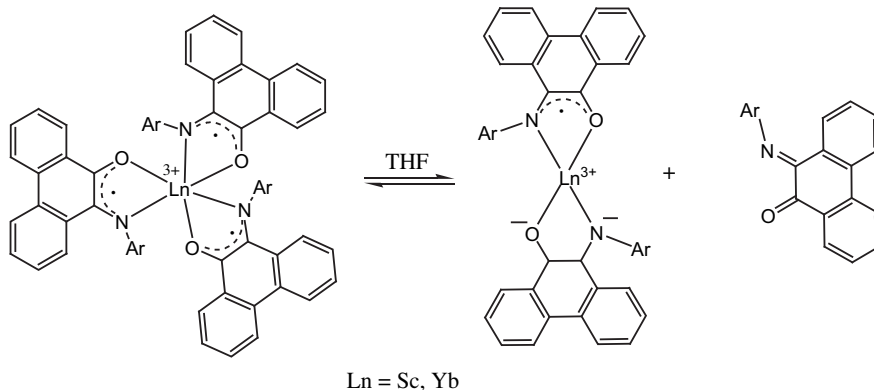


Fig. 1. Molecular structure of tris[N-(2,6-di-isopropylphenyl)phenanthren-*o*-iminosemiquinonate] of Ln (Ln = Yb (**2**), Dy (**5**), Ar = 2,6-di-isopropylphenyl).

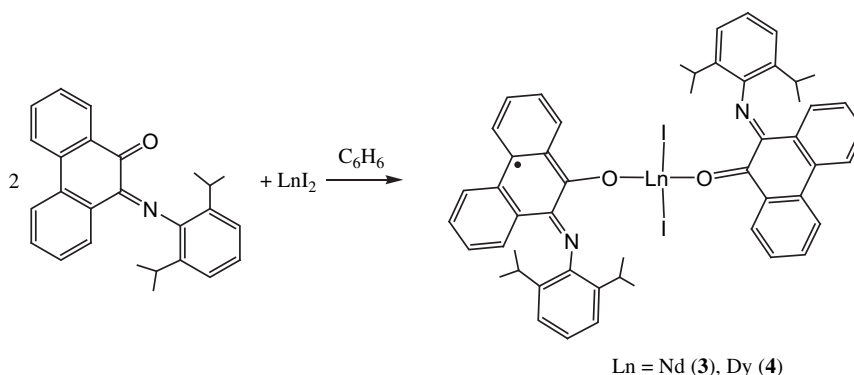
Table 2  
Selected bond lengths and angles for **2** and **5**.

Distance	<b>2</b> (Yb)	<b>5</b> (Dy)	Angle	<b>2</b> (Nd)	<b>5</b> (Dy)
Ln(1)–O(1)	2.164(7)	2.227(2)	O(1)–Yb(1)–N(1)	69.8(3)	68.97(7)
Ln(1)–O(2)	2.177(7)	2.231(2)	O(2)–Yb(1)–N(2)	69.5(3)	67.88(7)
Ln(1)–O(3)	2.155(8)	2.216(2)	O(3)–Yb(1)–N(3)	67.7(3)	65.41(7)
Ln(1)–N(1)	2.348(9)	2.390(2)	O(3)–Yb(1)–O(1)	84.0(3)	87.17(7)
Ln(1)–N(2)	2.400(10)	2.423(2)	O(1)–Yb(1)–O(2)	150.2(3)	146.36(7)
Ln(1)–N(3)	2.402(7)	2.549(2)	O(1)–Yb(1)–O(2)	125.5(3)	126.46(7)
O(1)–C(1)	1.320(17)	1.291(3)	O(3)–Yb(1)–N(1)	95.4(3)	80.59(7)
O(2)–C(27)	1.284(12)	1.295(3)	O(1)–Yb(1)–N(1)	69.8(3)	68.97(7)
O(3)–C(53)	1.293(14)	1.303(3)	O(3)–Yb(1)–N(2)	119.0(3)	122.83(8)
N(1)–C(2)	1.362(12)	1.350(3)	C(1)–O(1)–Yb(1)	118.7(6)	119.44(17)
N(2)–C(28)	1.375(11)	1.353(4)	C(27)–O(2)–Yb(1)	119.9(5)	123.17(18)
N(3)–C(54)	1.354(14)	1.331(3)	C(53)–O(3)–Yb(1)	124.7(7)	125.08(17)
C(1)–C(2)	1.377(15)	1.446(4)	O(1)–C(1)–C(2)	122.2(10)	119.0(2)
C(27)–C(28)	1.376(11)	1.451(4)	O(2)–C(27)–C(28)	121.1(7)	118.8(3)
C(53)–C(54)	1.445(16)	1.437(4)	O(3)–C(53)–C(54)	119.2(10)	118.7(2)



### 3.2. Reactions of $NdI_2$ and $DyI_2$ with phenanthren-*o*-iminoquinone

Recently we have found that diiodides  $LnI_2$  of Nd(II) and Dy(II) possess extremely high reductive ability [20]. Due to this property they easily react with phenanthren-*o*-iminoquinone L in benzene to give dark brown solutions from which diiodide-phenanthren-*o*-iminoquinonates  $I_2Nd(L)_2$  (**3**) and  $I_2Dy(L)_2$  (**4**) were isolated in 65% and 24% yield, respectively.



In the reaction of  $DyI_2$  partial disproportionation of **4** occurs resulted in formation of  $DyI_3$  and homoleptic complexes  $Dy(L)_3$  (**5**) in 14% yield. Judging by formation of  $NdI_3$  in the reaction with  $NdI_2$ , disproportionation of **3** also takes place but attempts to isolate  $Nd(L)_3$  failed. Then the reactions were carried out in ether the products **3** and **4** were isolated as complexes with two coordinated molecules of the solvent  $I_2Ln(L)_2(Et_2O)_2$  ( $Ln = Nd$  (**6**),  $Dy$  (**7**)) structure of which as well as structure of **5** have been determined by the X-ray diffraction analysis. The complexes **6** and **7** can be obtained also by crystallization of **3** and **4** from ether. The charge balance in **3**, **4**, **6** and **7** indicates that one of L ligands in these complexes bearings  $-1$  charge but the other one is neutral. Presence of a neutral coordinately bonded phenanthren-*o*-iminoquinone L is confirmed by its isolation upon dissolution of the complexes in acetonitrile: the solutions immediately get characteristic for solutions of L deep blue color and the  $^1H$  NMR spectra show the signals of free phenanthren-*o*-iminoquinone.

It was found that **6** and **7** have unprecedented for phenanthren-*o*-iminoquinonates type of metal–ligand coordination. In contrast to all known phenanthren-*o*-iminoquinonate complexes, which contain chelate  $M(-OCCN-)$  groups, in the isostructural compounds **6** and **7** both L ligands are bonded to metal atom in  $\eta^1$  fashion via O atom (Fig. 2, Table 3).

The Ln atoms in **6** and **7** lie in the inversion center in crystals. This stipulates identity of geometric characteristics of both L ligands and does not allow distinguishing the charged and neutral ligands. In addition, accuracy of the analysis is decreased because of low quality of the crystals. Nevertheless, main geometrical parameters of the molecules have been determined quite reliably. The C–O, C–N and C–C bond lengths in phenanthren ligands have middle values between those in free phenanthren-*o*-iminoquinone

and phenanthren-*o*-iminoquinonates. Metal atoms are located in the centre of tetragonal bipyramid, basal plane of which is formed by trans-located I atoms and O atoms of iminoquinone ligands. Apical positions are occupied by O atoms of molecules of coordinated ether. The Ln atoms are located exactly on the  $I(1)O(1)I(1)O(1)$  plane (deviation is 0.0 Å). The  $\eta^1$  coordination mode of L ligands is surely affirmed by great distances between N and Ln atoms (4.263 Å for Nd–N and 4.191 Å for Dy–N) which exclude possibility of any interaction. Such geometry of  $LnOCCN$  fragments is achieved due to increase of  $Ln-O-C(\text{iminoquinone})$  angles in complexes **6**, **7** on  $52$ – $58^\circ$  as compared with corresponding angles in **2** and in the complexes  $Mn(L)_2$  [8] and  $Re(L)_2$  [9]. The reasons which cause the absence of  $Ln...N$  interactions presumably are repulsion between lone pairs of nitrogen and iodine atoms, on the one hand, and sterical repulsion between 2,6-di-isopropylphenyl groups and iodine atoms, on the other hand. In accordance with this assumption the  $N...I$  distances (3.493 for **6** and 3.445 Å for **7**) were found to be shorter than the sum of  $vDw$  radii (3.7 Å [21]). It should be noted that  $\eta^1$  type of metal–ligand coordination in **6** and **7** does not lead to shortening of  $Ln-O(1)$  bonds as compared to **2**. The  $Ln-O(1)$  distances are 2.294(5) and 2.195(3) Å respectively in **6** and **7** whereas the  $Yb(1)-O(1,2,3)$  distances in **2** vary in the range of 2.155(8)–2.177(7) Å ( $R_{ion}(Nd^{3+}) = 0.983$  Å,  $R_{ion}(Dy^{3+}) = 0.912$  Å,

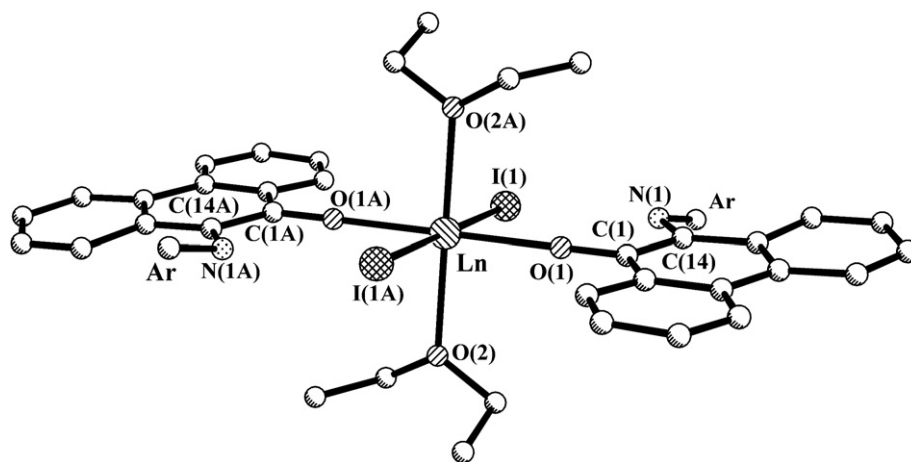


Fig. 2. Molecular structure of **6** (Nd) and **7** (Dy).

$R_{\text{ion}}(\text{Yb}^{3+}) = 0.868 \text{ \AA}$ , [22]). Other geometrical characteristics of considered fragments in **6** and **7** practically coincide with analogue parameters of chelate fragments in **2** and the mentioned complexes of Mn and Re.

Effective magnetic moments of **3** ( $3.2 \mu_{\text{B}}$ ) and **6** ( $3.4 \mu_{\text{B}}$ ) unambiguously say that  $\text{Nd}^{2+}$  ( $\mu_{\text{eff}} 2.9 \mu_{\text{B}}$ ) in the reaction is oxidized to  $\text{Nd}^{3+}$  ( $\mu_{\text{eff}} 3.68 \mu_{\text{B}}$  [23]) and that unpaired electrons on the radical ligands do not influence on total paramagnetism of the complexes. We believe that in these compounds unpaired electron of a charged ligand does not delocalized on the OCCN fragment but is located at metha-C atom (indicated in chart). Similar localization of unpaired electron at metha-C atom (relatively to CO group) in the radical phenanthren-*o*-iminoquinonate ligand has been described previously by Wieghardt [24] and is consistent with the structure of **6**. Absence of investment of spins of the radical ligands into total magnetic moments of **3** and **6** can be explained by existence of quick in NMR time scale intramolecular interligand electron transfer (LL'IT) which results in loss of paramagnetism of the ligands.

This assumption is confirmed by IR spectra of **3** and **6** that do not contain the absorption band at about 2500 nm, which is present in the spectra of iminoquinonate complexes with slow LL'IT but is absent in the compounds with quick LL'IT [10].

In the case of Dy complexes magnetic measurements gave close values for the products **4** ( $10.4 \mu_{\text{B}}$ ) and **7** ( $10.7 \mu_{\text{B}}$ ) but noticeably greater for **5** ( $13.8 \mu_{\text{B}}$ ). Accuracy of a method [15] used herein for magnetic measurement (5%) is essentially higher than the found deviations of  $\mu_{\text{eff}}$  and cannot be used for explanation of the obtained results. We suggest that (i) all three complexes contain  $\text{Dy}^{3+}$  cation ( $4f^9$ ,  $\mu_{\text{eff}} 10.6$  [23]), (ii) the complexes **4** and **7** have the same arrangement and electronic state as **3** and **6** respectively, (iii) in the compound **5** there are three radical phenanthren-*o*-iminoquinonate  $\text{L}^{\cdot-}$  ligands, spins of which do not change with each other and with  $\text{Dy}^{3+}$  paramagnetic center (the system is similar to that in **1**).

All the Nd and Dy complexes in solutions do not give EPR signals because of the presence of strong paramagnetic  $\text{Ln}^{3+}$  ions. The  $^1\text{H}$  NMR spectrum of **3** in benzene- $\text{D}_6$  displays only 9 broadened and

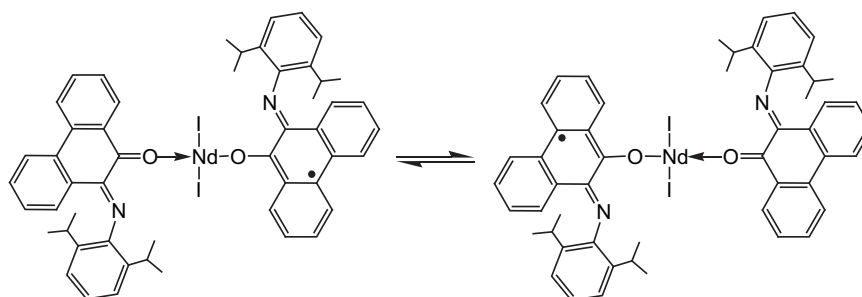


Table 3  
Selected bond lengths (Å) and angles (deg) for complexes **7** and **8**.

Distance	<b>6</b> (Nd)	<b>7</b> (Dy)	Angle	<b>6</b> (Nd)	<b>7</b> (Dy)
Ln(1)–O(1)	2.294(5)	2.195(3)	O(1)–Ln(1)–O(1A)	180.0	180.0
Ln(1)–O(2)	2.424(5)	2.330(3)	I(1)–Ln(1)–I(1A)	180.0	180.0
Ln(1)–I(1)	3.1068(7)	3.0380(4)	O(1)–Ln(1)–I(1)	85.65(14)	86.79(8)
O(1)–C(1)	1.295(9)	1.318(5)	O(1A)–Ln(1)–I(1)	94.35(14)	93.21(8)
N(1)–C(14)	1.355(10)	1.378(5)	O(2)–Ln(1)–I(1)	89.38(13)	88.50(9)
N(1)–C(15)	1.453(11)	1.441(6)	O(2A)–Ln(1)–I(1)	90.62(13)	91.50(9)
C(1)–C(14)	1.432(12)	1.409(7)	C(1)–O(1)–Ln(1)	176.6(5)	176.0(3)
			O(1)–C(1)–C(14)	119.4(7)	119.8(4)
			N(1)–C(14)–C(1)	114.0(7)	115.3(4)

shifted signals of nonequivalent protons of aromatic rings (2 of the signals are superimposed). These data do not allow to distinguish a charged and a neutral L ligands in the complex probably because of the same cause which stipulates identity of these groups in the X-ray analysis. In THF- $\text{D}_4$  solution the region of the spectrum becomes narrower as compared with the spectrum in benzene and additionally appeared a set of peaks of free phenanthren-*o*-iminoquinone.

#### 4. Conclusions

In summary, this work presents the synthesis and characterization of the first iminoquinonate complexes of rare earth metals. It was

found that homoleptic Ln(L)<sub>3</sub> compounds of Sc(III), Yb(III) and Dy(III) have a characteristic to iminosemiquinonates structure with O,N-chelated radical anion ligands. Magnetic measurements revealed that in the complexes of Sc (**1**) and Dy (**5**) spines of paramagnetic units are uncoupled while in the complex of Yb (**2**) there is antiferromagnetic interaction between unpaired electrons on the ligands and Yb<sup>3+</sup> cation. In the complexes I<sub>2</sub>Nd(L)<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub> (**6**) and I<sub>2</sub>Dy(L)<sub>2</sub>(Et<sub>2</sub>O)<sub>2</sub> (**7**), which are formed in the reactions of NdI<sub>2</sub> and DyI<sub>2</sub> with phenanthren-*o*-iminoquinone, both L ligands coordinate to metal center in quite unusual for iminoquinonates η<sup>1</sup> fashion via O atom. Due to high symmetry of the molecules the X-ray analysis does not allow to distinguish a charged and a neutral ligands. Structural data and magnetic measurements suggest that in these compounds as well as in the ether free complexes I<sub>2</sub>Nd(L)<sub>2</sub> (**3**) and I<sub>2</sub>Dy(L)<sub>2</sub> (**4**) there is a quick in NMR time scale intramolecular interligand reversible electron transfer. Odd structural arrangement and magnetic behavior of the obtained complexes challenge further investigation of rare earth iminoquinonates. This work now is under progress.

### Acknowledgment

This work was partially supported by the Russian Foundation for Basic Research (Grants Nos. 09-03-97016, 10-03-00190, 09-03-97034).

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