ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 12, pp. 852–857. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © T.V. Balashova, R.V. Rumyantsev, G.K. Fukin, A.P. Pushkarev, A.A. Maleev, D.B. Shpakovskii, T.A. Antonenko, E.R. Milaeva, M.N. Bochkarev, 2017, published in Koordinatsionnaya Khimiya, 2017, Vol. 43, No. 12, pp. 754–758.

Lanthanide Complexes with the Schiff Base Containing Sterically Hindered Phenol: Synthesis, Structure, and Luminescence Properties

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Received June 30, 2017

Abstract—The syntheses of the 2,6-di-*tert*-butyl-4-(2-hydroxybenzylideneamino)phenolate (L) complexes of Gd (**I**), Nd (**II**), Er (**III**), Yb (**IV**), Tm (**V**), Sm (**VI**), and Tb (**VII**) are described. The structures of the Gd and Er complexes are determined by X-ray diffraction analysis (CIF files CCDC nos. 1558820 (**I**) and 1558819 (**III**)). All synthesized compounds exhibit ligand-centered photoluminescence in a range of 405–485 nm. In addition, the luminescence spectra of solid samples of the neodymium and ytterbium complexes contain narrow bands of *f*–*f* transitions characteristic of Nd^{3+} and Yb^{3+} ions.

Keywords: lanthanides, Schiff base, photoluminescence, metal-centered emission

DOI: 10.1134/S1070328417120016

INTRODUCTION

Among potential areas of application of rare-earth metal compounds, the field of luminescent materials is one of the main ones due to the unique property of Ln^{3+} ions to generate the narrow-band emission of *f*–*f* transitions. The radiation wavelength can change from the near-UV to near-IR ranges depending on the lanthanide nature. In the recent time, luminescent materials emitting in the near-IR range attract serious attention, since they find use in fiber-optic lines of communication, planar fiber amplifiers, and IR detectors [1, 2], as well as for biomedical diagnostics and therapy [3, 4]. Since there are no materials emitting in the IR range among purely organic luminophores, researchers concentrated efforts on the search for complexes of 4*f*-metals (Nd, Er, Tm, and Yb) emitting in the range from 800 to 3000 nm. In these cases, the Schiff bases with biochemical and antimicrobial activity were often used as ligands in the complexes designed for the application in biomedical purposes [5]. In addition, molecules of these ligands, as a rule, contain sterically hindered phenol capable of forming phenoxyl radicals and playing an important role in the antioxidant activity of the complexes formed [6, 7]. It should be mentioned that many drugs used as metal complexes exhibit a higher activity compared to the purely organic substrates [8].

The chelates with the Schiff base containing 2,6-di-*tert*-butylphenol have previously been obtained for some transition metals, in particular, Cu(II), Co(II), Zn(II) [9, 10], Pd [11, 12], and Cd [13]. It has been shown for the cadmium and palladium derivatives that the biological activity of the compounds is significantly determined by the ligand environment of the metal. It seemed interesting to synthesize and study the luminescence properties of lanthanide complexes containing similar ligands.

EXPERIMENTAL

The syntheses were carried out under the conditions excluding contact with air oxygen and moisture using the standard Schlenk techniques. Diethyl ether and tetrahydrofuran were dried with sodium benzophenone ketyl, whereas hexane and pentane were dried over sodium (using standard procedures). The dried solvents were sampled in vacuo prior to use. Tetrahydrofuran (THF, for spectral studies) was purified by the treatment with NdI_2 as described previously [14]. The silylamide complexes of lanthanides $Ln[N(SiMe_3)_2]_3$ were synthesized using a known procedure [15]. The ligand 2,6-di-*tert*-butyl-4-(2-hydroxybenzylideneamino)phenol (HL) was synthesized according to a described procedure [9].

IR spectra were recorded on an FSM-1201 FT-IR spectrometer in a range of 4000–400 cm^{-1}. The samples were prepared as suspensions in Nujol. Absorption spectra were measured on a PerkinElmer 577 spectrometer. A PerkinElmer LS-55 spectrometer was used to detect emission spectra in a range of 200–

800 nm. The C,H,N-elemental analyses were carried out on an Elementar Vario ELcube Analyzer instrument. The spectra and efficiency in the IR range were determined on a NIR-512 spectrometer (Ocean Optics) calibrated by an LS-1 CAL lamp (Ocean Optics).

Synthesis of $[Gd(L)_3]_2$ (I). A solution of HL (104 mg, 0.320 mmol) in diethyl ether (10 mL) was added to a solution of $Gd[N(SiMe_3)_2]_3$ (68 mg, 0.107 mmol) in diethyl ether (5 mL). The reaction mixture was stirred for 30 min at room temperature. Diethyl ether and other volatile reaction products were removed by condensation in vacuo. The remained oily substance was recrystallized from hexane. The yield of complex **I** as yellow crystals was 80 mg (67%).

For $C_{126}H_{156}N_6O_{12}Gd_2$				
Anal. calcd., %	C, 66.93	H, 6.95	N, 3.72	Gd, 13.91
Found, %	C, 66.89	H, 6.91	N, 3.79	Gd, 13.88

IR (ν, cm^{-1}): 3631 (m), 1608 (s), 1541 (w), 1378 (s), 1346 (s), 1324 (w), 1246 (w), 1230 (m), 1177 (w), 1145 (s), 1116 (w), 1064 (s), 1026 (w), 966 (m), 918 (w), 889 (w), 871 (w), 853 (w), 823 (w), 808 (w), 782 (w), 753 (m), 738 (m), 670 (w), 644 (w), 631 (w), 597 (m), 564 (w), 500 (m).

Synthesis of $[Yb(L)_3]_2$ (IV). A solution of HL (125 mg, 0.384 mmol) in hexane (10 mL) was added to a solution of $Yb[N(SiMe_3)_2]_3$ (84 mg, 0.128 mmol) in hexane (5 mL). The reaction mixture was stirred for 30 min at room temperature. Hexane and other volatile products were removed by condensation in vacuo. The remained oily substance was crystallized from pentane. The yield of complex **IV** as orange crystals was 106 mg (72%).

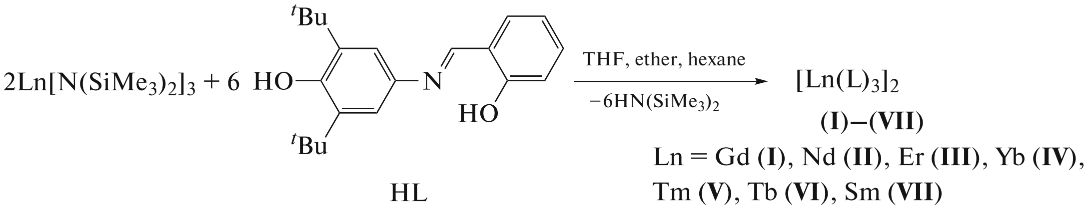
For $C_{126}H_{156}N_6O_{12}Yb_2$				
Anal. calcd., %	C, 66.01	H, 6.86	N, 3.67	Yb, 15.09
Found, %	C, 66.09	H, 6.85	N, 3.71	Yb, 15.07

Complexes $[Nd(L)_3]_2$ (**II**), $[Er(L)_3]_2$ (**III**), $[Tm(L)_3]_2$ (**V**), $[Sm(L)_3]_2$ (**VI**), and $[Tb(L)_3]_2$ (**VII**) were synthesized similarly. The IR spectra of the products were identical to the spectrum of complex **I**. The crystals of complex **III** suitable for X-ray diffraction analysis were obtained by the reaction in THF followed by the recrystallization of the product from pentane.

X-ray diffraction analyses of complexes **I** and **III** were carried out on an Oxford Xcalibur Eos automated diffractometer (graphite monochromator, MoK_α radiation, ω scan mode, $\lambda = 0.71073$ Å). Experimental arrays of intensities were integrated using the CrysAlisPro program [16]. The SCALE3 ABSPACK program [17] was used to apply absorption corrections. The structures were solved by a direct method (SHELXTL) [18] and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and refined in the riding model. The main crystallographic characteristics and X-ray diffraction experimental parameters for complexes **I** and **III** are presented in Table 1. In the unit cell of complex **I**, 1.5 Et_2O molecules and 0.8 molecule of hexane disordered over several positions fall onto every two molecules of complex **I**. In turn, two THF molecules and three pentane molecules fall onto every two molecules of complex **III**. Selected bond lengths and angles are given in Table 2. The coordinates of atoms and other parameters of the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1558820 (**I**) and 1558819 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The target complexes were synthesized by the reactions of the free Schiff base (HL) with trimethylsilylamides of the corresponding rare-earth metals in a ratio of 1 : 3. The reactions occur readily at room temperature in THF, diethyl ether, or hexane and afford the expected products as yellow or orange finely crystalline powders in 67–83% yields.



Ln = Gd (**I**), Nd (**II**), Er (**III**), Yb (**IV**), Tm (**V**), Tb (**VI**), Sm (**VII**)

The X-ray diffraction analyses show that complexes **I** and **III** are dimeric compounds with the identical molecular structures. Each Ln atom is coordinated by two terminal and two bridging L ligands through the bidentate mode (Fig. 1). As a result, the coordination number of the Gd atoms in complex **I** and Er atoms in complex **III** is equal to 7. The coordination polyhedron of the Ln atoms in compounds **I** and **III** is a distorted pentagonal bipyramid. As it should be expected, the terminal Gd–O and Er–O

Table 1. Selected crystallographic characteristics and X-ray diffraction experimental parameters for complexes **I** and **III**

Parameter	Value	
	I	**III**
Empirical formula*	$C_{131.40}H_{169.10}N_6O_{12.75}Gd_2$	$C_{137.50}H_{182}Er_2N_6O_{13}$
FW	2351.13	2461.41
Temperature, K	100(2)	100(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell parameters:		
a, Å	15.39683(15)	15.40580(10)
b, Å	18.04056(17)	18.21820(10)
c, Å	25.4620(3)	25.5074(5)
α, deg	73.5707(8)	106.7000(10)
β, deg	85.4029(8)	104.6290(10)
γ, deg	79.4417(8)	99.3930(10)
V, Å^3	6665.88(11)	6416.49(14)
Z	2	2
ρ_{calcd}, mg/m^3	1.171	1.274
μ, mm^{-1}	1.043	1.360
Crystal size, mm	0.70 × 0.40 × 0.20	0.40 × 0.20 × 0.05
F(000)	2459	2578
θ, deg	3.05–28.00	3.05–26.00
Number of reflections collected/independent	126446/32100	96729/24995
R_{int}	0.0335	0.0412
Number of reflections with $I > 2\sigma(I)$	26719	20704
R_1, wR_2 ($I > 2\sigma(I)$)	0.0440, 0.1065	0.0348, 0.0823
R_1, wR_2 (for all data)	0.0591, 0.1124	0.0459, 0.0885
S	1.053	1.060
Residual electron density (max/min), *e*/Å^3	2.529/–2.150	1.420/–1.015

* The empirical formulas for complexes **I** and **III** were calculated taking into account solvate molecules of the solvents.

Table 2. Selected distances (Å) and angles (deg) in complexes **I** and **III**

Bond	**I**	**III**	Bound and angle	**I**	**III**
Ln–O_{term}	2.1993(17)–2.2328(16)	2.1549(17)–2.1767(15)	Ln(1)–Ln(2)	3.83252(17)	3.76812(15)
Ln–μ_2-O	2.3040(16)–2.4227(17)	2.2566(15)–2.3548(16)	Ln(1)$_{\mu2}$-OLn(2)	106.39(6), 110.49(6)	108.21(5), 111.11(6)
Ln–N	2.5518(18)–2.638(2)	2.492(2)–2.587(2)	O(1^x)LnN(1^x)	68.49(6)–74.76(6)	69.23(6)–75.97(6)

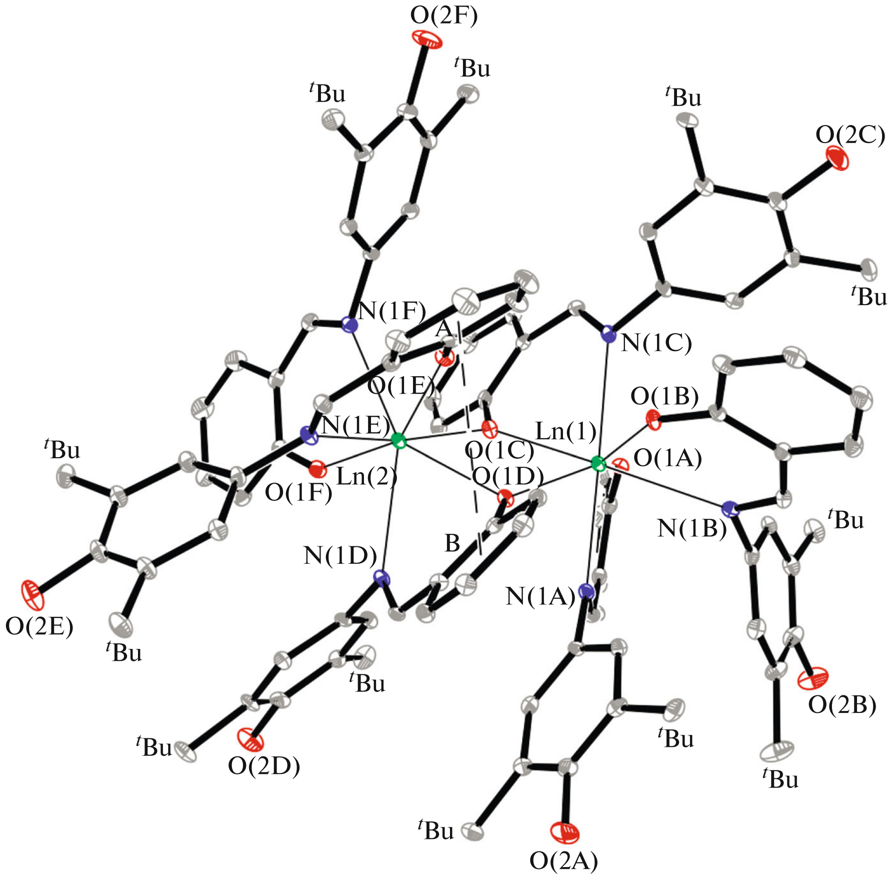


Fig. 1. Molecular structures of complexes **I** (Ln = Gd) and **III** (Ln = Er). Thermal ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity.

distances are noticeably shorter than the bridging distances (Table 2). The Gd–N distances in complex **I** and Er–N in complex **III** are 2.5518(18)–2.638(2) and 2.492(2)–2.587(2) Å, respectively. The Ln(1)···Ln(2) distances are equal to 3.83252(17) for Gd and 3.76812(15) Å for Er. These geometric characteristics are typical of the related gadolinium and erbium complexes [19–21]. The central four-membered fragments Ln(1)O(1C)Ln(2)O(1D) in complexes **I** and **III** are nonplanar: the dihedral angles between the planes O(1C)Ln(1)O(1D) and O(1C)Ln(2)O(1D) are 16.25° and 12.20° for compounds **I** and **III**, respectively.

Rings A and B (Fig. 1) in complexes **I** and **III** are unfolded relative to each other by 14.04° and 22.14°, respectively. The distance between the centers of rings A and B is 3.871 Å in complex **I** and 4.016 Å in complex **III**. These values assume the existence of a $\pi\cdots\pi$ interaction in the indicated fragments [22].

The absorption spectra of THF solutions of complexes **I–VII** at room temperature (Fig. 2) exhibit a band at 202–214 nm caused by the E_2 transition, a band at 235 nm caused by the *K* transition, and a band at 273 nm caused by the *B* transition, as well as n–π^* bands in a range of 350–370 nm.

All synthesized compounds in a THF solution exhibit photoluminescence of the ligands as a broadened band at 405–485 nm (Fig. 3) upon excitation with the light with λ_{exc} = 350–370 nm.

The triplet level of the ligand was determined from the low-temperature photoluminescence spectrum of the gadolinium complex (Fig. 4). The low position of the triplet level of the studied ligand (18020 cm^{-1}) allowed one to expect that the latter could be a good sensitizer of luminescence for the IR-emitting lanthanides. According to this assumption, it has been found that the photoluminescence spectra of the Nd and Yb complexes with the HL ligand contain bands of metal-centered emission characteristic of the corresponding Ln^{3+} ions (Fig. 5).

Thus, the Gd, Nd, Er, Yb, Tm, Sm, and Tb complexes with 2,6-di-*tert*-butyl-4-(2-hydroxybenzylideneamino)phenol were synthesized for the first time, and their luminescence properties were studied. The neodymium and ytterbium complexes exhibit metal-centered emission in the near-IR range caused by the *f*–*f* transitions characteristics of Nd^{3+} and Yb^{3+} ions,

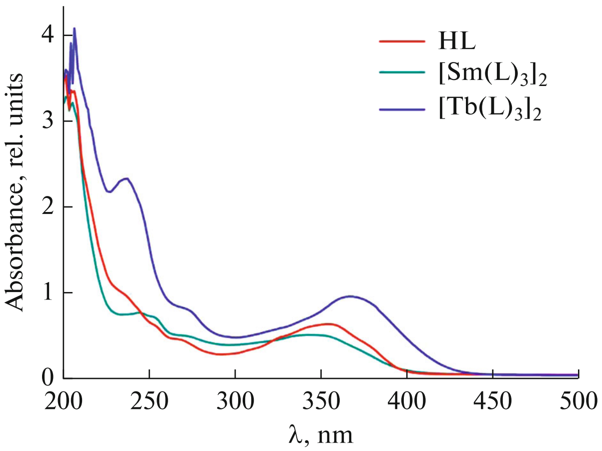


Fig. 2. Absorption spectra of the HL ligand and the $[Sm(L)_3]_2$ and $[Tb(L)_3]_2$ complexes in THF solutions at room temperature (10^{-5} mol/L).

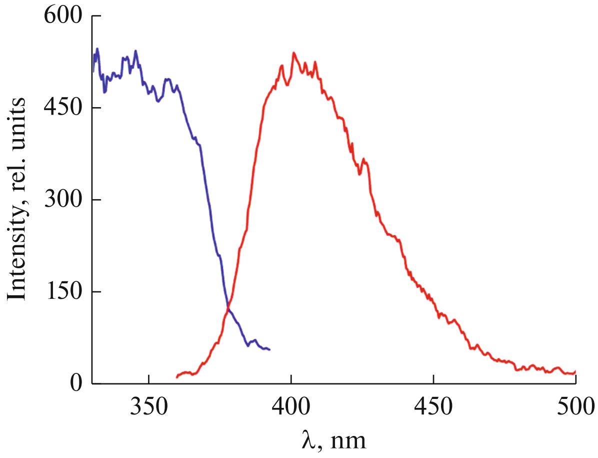


Fig. 3. Photoluminescence spectrum of the $[Sm(L)_3]_2$ complex (λ_{exc} = 350 nm) in a THF solution.

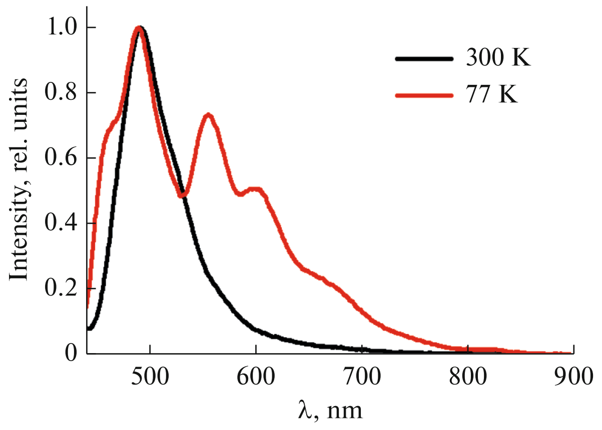


Fig. 4. Photoluminescence spectra of the $[Gd(L)_3]_2$ complex at room temperature and at 77 K.

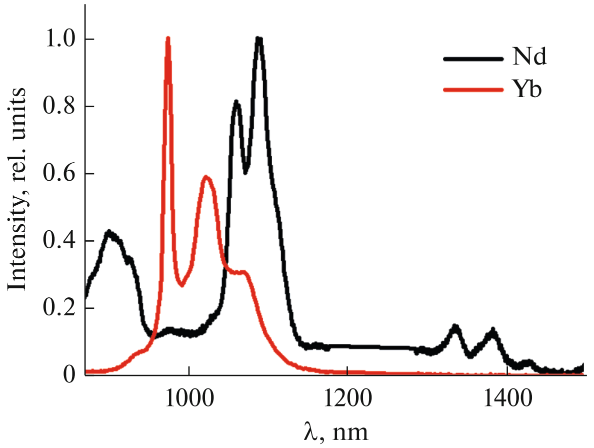


Fig. 5. Photoluminescence spectra of the solid samples of $[Ln(L)_3]_2$ (Ln = Nd and Yb, λ_{exc} = 405 nm).

which allows their application in bioimaging. Since the decreased hydrolytic stability of the synthesized compounds prevents their use for the purposes indicated, attempts to modify them are being made at the present time.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, projects no. 16-03-00129 and 16-33-00056.

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Translated by E. Yablonskaya