ISSN 1070-3632, Russian Journal of General Chemistry, 2016, Vol. 86, No. 5, pp. 1209–1211. © Pleiades Publishing, Ltd., 2016.
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LETTERS TO THE EDITOR

Synthesis and Luminescent Properties of Coordination Compounds of Europium(III), Gadolinium(III), and Terbium(III) with *para*-Alkyloxybenzoic Acids

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Received September 17, 2015

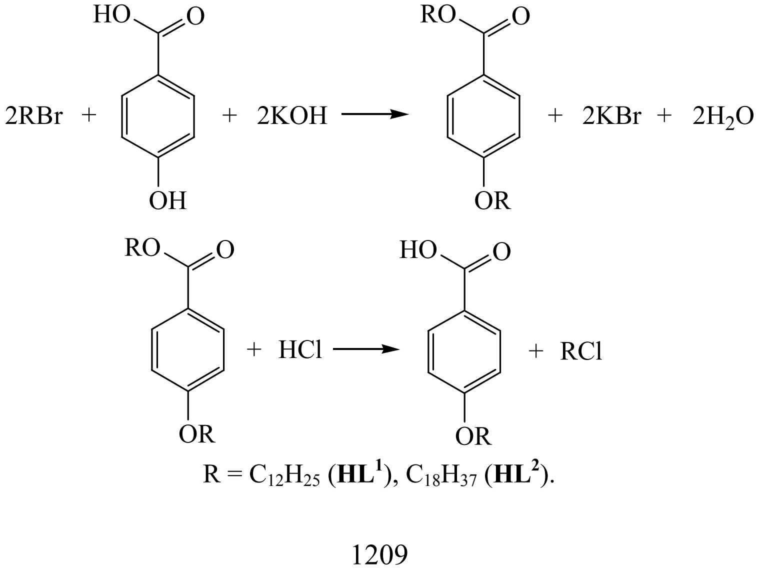
Keywords: *para*-alkoxybenzoic acid, lanthanide, luminescence

DOI: 10.1134/S1070363216050418

It is well known that coordination compounds of lanthanides with aromatic carboxylic acids display efficient luminescent properties in the visible and near-infrared ranges [1]. We have earlier prepared a number of complexes with promising luminescent properties [2, 3]. However, the majority of the compounds were poorly soluble in organic media; that limited their possible application. One of the ways to enhance the complexes solubility in nonpolar organic solvents is the use of aromatic carboxylic acids with alkyl substituents as the ligands. Moreover, the improved film-forming properties and the amphiphilic nature of the compounds containing long-chain substituents will open the possibility of the molecular films preparation via the Langmuir–Blodgett technology.

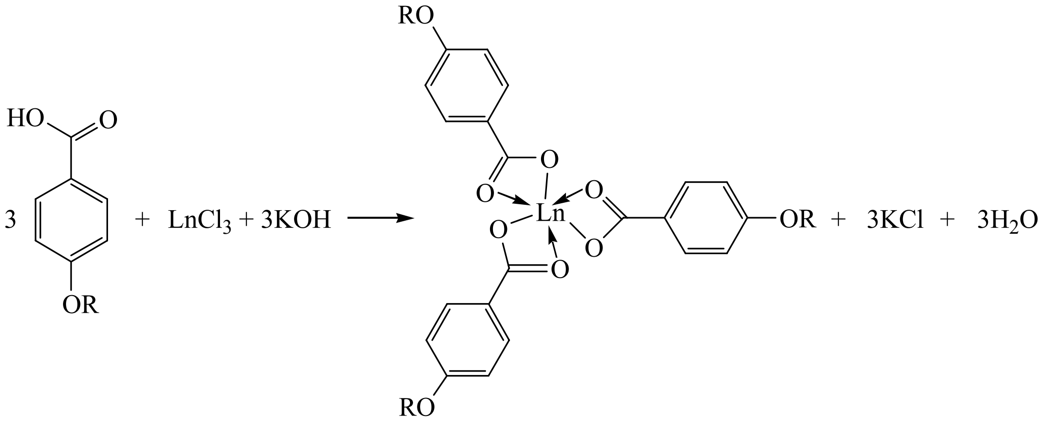
In view of the above, we synthesized coordination compounds of europium(III), gadolinium(III), and terbium(III) with *para*-dodecyloxybenzoic (**HL^1**) and *para*-octadecyloxybenzoic (**HL^2**) acids. The ligands were prepared via the reaction of the corresponding alkyl bromides with *para*-oxybenzoic acid in the presence of potassium hydroxide, followed by hydrolysis of the intermediate ester (Scheme 1).

Scheme 1.



R = $C_{12}H_{25}$ (**HL^1**), $C_{18}H_{37}$ (**HL^2**).

Scheme 2.



R = $C_{12}H_{25}$, Ln = Eu^{3+} (**1**); R = $C_{12}H_{25}$, Ln = Tb^{3+} (**2**); R = $C_{12}H_{25}$, Ln = Gd^{3+} (**3**); R = $C_{18}H_{37}$, Ln = Eu^{3+} (**4**); R = $C_{18}H_{37}$, Ln = Tb^{3+} (**5**); R = $C_{18}H_{37}$, Ln = Gd^{3+} (**6**).

Synthesis of complexes **1–6** was performed via reaction of the prepared *para*-alkoxybenzoic acids with europium(III), gadolinium(III), or terbium(III) chloride in an alkaline medium. Yield of the complexes was of 55–71% (Scheme 2).

The prepared coordination compounds and the starting acids were white powders, readily soluble in chloroform. According to the elemental analysis data (Table 1), composition of complexes **1–6** matched the general formula LnL_3.

In contrast to the ligands, IR spectra of the prepared complexes (see table) did not contain a group of the bands at 2800–2400 cm^{-1} assigned to the dimers of carboxylic acids. Moreover, the band of stretching vibrations of C=O bond (1686 cm^{-1}) was also absent, evidencing anionic form of the acids in the complex. Since the difference ($\Delta\nu$) between the asymmetric and symmetric vibrations of the carboxylic group stretching was of 156–183 cm^{-1} (<220 cm^{-1}), bidentate coordination of the acid anions could be suggested [4]. The spectra of the synthesized complexes **1–6** contained no band of coordinated water hydroxyl; the absence of water was further confirmed by the data of elemental analysis. The anhydrous nature of the complexes could be explained by the hindrance effect of the long-chain substituents making impossible introduction of water molecules at the inner coordination sphere of the lanthanide ions.

Phosphorescence spectra of gadolinium complexes has been generally used for the determination of the energy of excited triplet levels (T_1) of the ligands, since phosphorescence of the Gd^{3+} ion is caused by the transfer of the ligand molecule from excited triplet state to the ground singlet [1]. From the luminescence spectra of the gadolinium complexes with *para*-dodecyloxybenzoic and *para*-octadecyloxybenzoic acids, the energies of excited triplet levels of the acid anions were of 20441 and 20047 cm^{-1}, respectively.

Yields and the data of elemental analysis and IR spectroscopy for compounds **1–6**

Comp. no.	Yield, %	IR spectrum, cm^{-1}	Formula	Found, %			Calculated, %		
				C	H	Ln	C	H	Ln
1	65.3	1606 [$\nu_{as}(COO^-)$], 1425 [$\nu_s(COO^-)$]	$C_{57}H_{87}O_9Eu$	64.15	8.25	14.32	64.10	8.15	14.25
2	68.4	1610 [$\nu_{as}(COO^-)$], 1435 [$\nu_s(COO^-)$]	$C_{57}H_{87}O_9Tb$	63.75	8.17	14.90	63.69	8.10	14.80
3	71.2	1605 [$\nu_{as}(COO^-)$], 1423 [$\nu_s(COO^-)$]	$C_{57}H_{87}O_9Gd$	63.89	8.23	14.75	63.81	8.12	14.65
4	55.4	1609 [$\nu_{as}(COO^-)$], 1429 [$\nu_s(COO^-)$]	$C_{75}H_{123}O_9Eu$	68.32	9.41	11.58	68.23	9.33	11.52
5	57.5	1612 [$\nu_{as}(COO^-)$], 1431 [$\nu_s(COO^-)$]	$C_{75}H_{123}O_9Tb$	67.97	9.32	12.02	67.87	9.28	11.99
6	61.8	1601 [$\nu_{as}(COO^-)$], 1417 [$\nu_s(COO^-)$]	$C_{75}H_{123}O_9Gd$	68.05	9.35	11.97	67.98	9.29	11.86

The energy difference between the T_1 term of the ligand and the $^5D_4$ one of Tb^{3+} ion (20500 cm^{-1}) in the 2500–4000 cm^{-1} range has been found optimal for the intermolecular transfer of excitation energy from organic ligand to lanthanide ion [5]. In the studied case, the resonance term of Tb^{3+} ion was higher in energy than the triplet levels of *para*-dodecyloxybenzoate and *para*-octadecyloxybenzoate anions; therefore, luminescence was not observed for those complexes.

Similarly, for Eu^{3+} complexes, the optimal energy gap between the T_1 term of the ligand and the $^5D_0$ term (17200 cm^{-1}) of Eu^{3+} ion should fall in the 2500–3500 cm^{-1} range [5]. In the studied case, it was of 3241 cm^{-1} for europium(III) *para*-dodecyloxybenzoate and of 2847 cm^{-1} for europium(III) *para*-octadecyloxybenzoate, matching the indicated limits. Therefore, the efficient excitation energy transfer from the ligands to Eu^{3+} ion should be operative for those complexes; that was confirmed by the experimental luminescence spectra. Moreover, the integral intensity of luminescence of europium(III) complex with *para*-dodecyloxybenzoic acid was 1.5 times higher than of that with *para*-octadecyloxybenzoate acid and 4.3 times higher than for europium(III) benzoate used as reference.

Synthesis of *para*-alkoxybenzoic acids was performed as described elsewhere [6]. The corresponding alkyl bromide was added to a solution of *para*-hydroxybenzoic acid (1.18 g) in 30 mL of ethanol, and then a solution of KOH (1.69 g in 60 mL of ethanol) was added dropwise. The reaction mixture was stirred at 60°C during 14 h. The precipitate was filtered off and dried at 80°C to constant mass.

***para*-Dodecyloxybenzoic acid (HL^1).** Yield 58.9%. IR spectrum, ν, cm^{-1}: 2700–2500 (O–H), 1673 (C=O). ^1H NMR spectrum, δ, ppm: 10.00 s (1H, COOH), 8.05 d (2H, H_{Ar}, J = 8.8 Hz), 6.94 (2H, H_{Ar}, J = 8.8 Hz), 4.04 t (2H, OCH_2, J = 6.6 Hz), 1.27–1.84 m (20H, CH_2), 0.88 t (3H, CH_3, J = 6.8 Hz). Found, %: C 74.55; H 9.75. $C_{19}H_{30}O_3$. Calculated, %: C 74.51; H 9.80.

***para*-Octadecyloxybenzoic acid (HL^2).** Yield 55.7%. IR spectrum, ν, cm^{-1}: 2700–2500 (O–H), 1670 (C=O). ^1H NMR spectrum, δ, ppm: 10.02 s (1H, COOH), 8.04 d (2H, H_{Ar}, J = 8.7 Hz), 6.92 (2H, H_{Ar}, J = 8.7 Hz), 4.01 t (2H, OCH_2, J = 6.6 Hz), 1.26–1.83 m (32H, CH_2), 0.87 t (3H, CH_3, J = 6.8 Hz). Found, %: C 76.97; H 10.82. $C_{25}H_{42}O_3$. Calculated, %: C 76.92; H 10.77.

Synthesis of complexes 1–6 was performed according to the procedure in [7]. An alcoholic solution of NaOH was added dropwise to an alcoholic solution of the ligand (3 mmol) to pH 6. Then, lanthanide chloride (1 mmol) in 5 mL of a 1 : 1 ethanol–water mixture was added dropwise to the reaction mixture at vigorous stirring. The solution with the formed precipitate was stirred during 1 h. The precipitate was filtered off, sequentially washed with distilled water and with ethanol, and dried at 80°C to constant mass.

^1H NMR spectra were registered using a JNM ECA 400 (JEOL) spectrometer. IR spectra were recorded using a Vertex 70 (Bruker) Fourier spectrometer equipped with an ATR attachment (4000–400 cm^{-1}). Elemental analysis (C, H) was performed using a Vario EL III (Elementar) analyzer; the metal content was determined via complexonometric titration. Luminescent spectra were obtained with a Flyuorat-02-Panorama spectrofluorimeter.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 14-03-00830) and the Ministry of Education and Science in the frame of the governmental contract (no. 007-01114-16 PR 0256-2014-0009).

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