ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 2, pp. 262–266. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © S.B. Meshkova, Z.M. Topilova, N.N. Devyatykh, A.N. Gusev, V.F. Shul'gin, 2011, published in Zhurnal Neorganicheskoi Khimii, 2011, Vol. 56, No. 2, pp. 301–305.

PHYSICAL METHODS OF INVESTIGATION

IR Luminescence of Neodymium(III) and Ytterbium(III) Ions in Complexes with N-Alkyl-Substituted 2-Aminobenzoic Acids

S. B. Meshkova[a], Z. M. Topilova[a], N. N. Devyatykh[a], A. N. Gusev[b], and V. F. Shul'gin[b]

[a] *Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine, Lyustdorfskaya doroga 86, Odessa, 65080 Ukraine*

[b] *Vernadsky Taurida National University, pr. Vernadskogo 4, Simferopol, 95007 Ukraine*

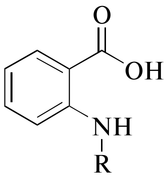
Received March 20, 2009

Abstract—The luminescence of neodymium(III) and ytterbium(III) ions in complexes with N-alkyl-substituted 2-aminobenzoic acids has been studied. The luminescence spectra of the Nd(III) complexes show two bands with maxima at 875 and 904 and 1060 nm, and the spectra of the Yb(III) complexes show one band at 980 nm. The introduction of an additional ligand or some surfactants into the Nd(III) and Yb(III) coordination sphere leads to an increase in the luminescence intensity. A correlation between the luminescence intensity of Nd(III) and Yb(III) 2(*N*-alkylamino)benzoates and the length of the hydrocarbon radical bound to the nitrogen atom has been studied.

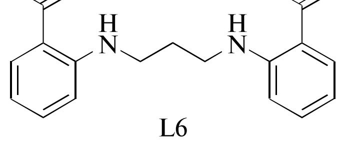
DOI: 10.1134/S0036023611020203

A powerful stimulus for synthesizing and studying lanthanide (Ln) complexes is the possibility to use them as the light-emitting component in optical diodes, organic light-emitting diodes (OLEDs) [1–4]. Lanthanide compounds with organic ligands exhibit narrow-band luminescence in both the visible (Pr, Sm, Eu, Tb, Dy, Tm) and infrared (Nd, Yb, Er) spectral ranges. In the first case, ligands absorbing UV light are used, whereas in the second case, ligands also absorbing visible light are used [5]. The luminescence of Nd(III) and Yb(III) in complexes with β-diketones [6, 7]; organic dyes [8], including porphyrins [9]; and some other organic ligands has been reported. To the best of our knowledge, no information is available on the luminescence of lanthanides in complexes with N-alkyl-substituted 2-aminobenzoic acids.

In this work, we studied spectral-luminescent properties of the Nd(III) and Yb(III) complexes with N-alkyl-substituted 2-aminobenzoic acids and searched for a relationship between the luminescence intensity and the ligand structure.



R = CH_3 (L1), C_2H_5 (L2), n-C_3H_7 (L3), n-C_4H_9 (L4), n-C_5H_{11} (L5)



L6

EXPERIMENTAL

N-Alkyl-substituted 2-aminobenzoic acids were obtained by oxidation of corresponding 1-alkylisatines by a 30% hydrogen peroxide solution [10]. Commercially available Ferak, Aldrich, or Sigma α,α'-dipyridyl (Dipy), 1,10-phenanthroline (Phen), bathophenanthroline (bathoPhen), trioctylphosphine oxide (TOPO), diantipyrylmethane (DAM), and its propyl and phenyl derivatives (DAPM and DAPhM) were used as additional ligands.

Initial 0.01 M solutions of N-alkyl-substituted 2-aminobenzoic acids and additional ligands were prepared by dissolving weighed samples of corresponding powders in ethanol. Initial 0.1 M Nd(III) and Yb(III) chloride solutions were prepared by dissolving their oxides (99.99%) in hydrochloric acid (1 : 1) followed by evaporation of its excess and dissolution of the residue in twice distilled water. The complexes were prepared by mixing a $NdCl_3$ ($YbCl_3$) solution with an N-alkyl-substituted 2-aminobenzoic acid solution in the presence of a buffer solution maintaining an optimal pH value, monitored with an OP-211/1 pH-meter (Hungary) equipped with an ESL-43-07 glass electrode and a silver/silver chloride reference electrode. A 4% urotropine solution was used as a buffer solution. Initial 0.01 M solutions of surfactants—cetyltrimethylammonium bromide (CTA), cetylpyridinium bromide (CPB), ethonium, Triton X-100, and Tween 80—were prepared by dissolving weighed samples in twice distilled water.

The neodymium complex with 2-(*N*-amylamino)benzoic acid was synthesized by the following procedure: 9 mmol of 2-(*N*-amylamino)benzoic acid was added to a solution of 9 mmol of NaOH in 10 mL of water. Then, 3 mmol of $NdCl_3 \cdot 6H_2O$ in 10 mL of water was added under magnetic stirring to the resulting solution. The reaction mixture was magnetically stirred for 1 h under moderate heating. The resulting precipitate was allowed to stand under the supernatant for 24 h and then filtered, washed with water, and dried in air. The yield of the product was 77% of the theoretically possible amount. According to elemental and thermal analysis data, the composition of the complex corresponds to the formula $Nd(L5)_3 \cdot 2H_2O$, where HL is 2-(*N*-amylamino)benzoic acid.

For $C_{63}H_{52}N_3NdO_8$ anal. calcd. (%): C, 54.13; H, 6.51; Nd, 18.05.

Found (%): C, 54.06; H, 6.22; Nd, 18.15.

IR ($\overline{\nu}_{max}$, cm^{-1}): 1616 ν_{as}(COO$^-$), 1396 ν_s(COO$^-$).

The heteroligand neodymium complex with 2-(*N*-amylamino)benzoic acid and 1,10-phenanthroline was obtained by the following procedure: to a solution of 3 mmol of neodymium 2-(*N*-amylamino)benzoate prepared by the above method, a solution of 3 mmol of 1,10-phenanthroline in 10 mL of ethanol was added under magnetic stirring. The resulting precipitate was allowed to stand under the supernatant for 24 h and then filtered, washed with water, and dried in air. The yield of the product was 74%. According to elemental and thermal analysis data, the complex has the composition $Nd(L5)_3 \cdot Phen \cdot 3H_2O$.

For $C_{48}H_{62}N_5NdO_9$ anal. calcd. (%): C, 57.83; H, 6.20; N, 7.03; Nd, 14.45.

Found (%): C, 57.69; H, 5.75; N, 7.36; Nd, 14.01.

IR ($\overline{\nu}_{max}$, cm^{-1}): 1615 ν_{as}(COO$^-$), 1425 ν_s(COO$^-$).

The IR spectra of samples recorded as pellets with KBr on a Nicolet Nexus 470 FT spectrophotometer in the range 400–4000 cm^{-1}. The absorption spectra were recorded on a Perkin-Elmer Lambda-9 UV-VIS-NIR spectrophotometer. The luminescence spectra were recorded on an LOMO SDL-1 diffraction spectrometer with an FEU-62 photomultiplier in the range 850–1090 nm for Nd(III) and 960–1000 nm for Yb(III). Luminescence was excited by the light of a DRSh-250 mercury lamp with the use of a UFS-2 light cutoff filter transmitting at $\lambda = 365$ nm. The Nd(III) luminescence intensity was measured for the luminescence maxima at 875 and 1060 nm, and the Yb(III) luminescence intensity was measured for the peak at 980 nm.

RESULTS AND DISCUSSION

The energies of the triplet T_1 levels of the ligands (Fig. 1) measured from the phosphorescence spectra (77 K) of Gd(III) 2-(*N*-alkylamino)benzoates are higher than the energies of the emitting $^4F_{3/2}$ (Nd(III)) and $^2F_{5/2}$ (Yb(III)) levels, so that the intramolecular energy transfer to these levels upon excitation into the ligand is in principle possible. Inasmuch as the Ln(III) ions in complexes with organic ligands exhibit luminescence owing to the intramolecular ligand-to-Ln energy transfer, it is important to know which radiation wavelength should be used for optimal excitation of the ligand. As follows from the absorption spectrum of the Nd(III) complex (Fig. 2a), the maximum light absorption of the compounds under consideration occurs at 300–380 nm. This is evidence that luminescence can be excited by the strong line of mercury at 365 nm with subsequent energy transfer from the ligand to the Nd(III) or Yb(III) ions.

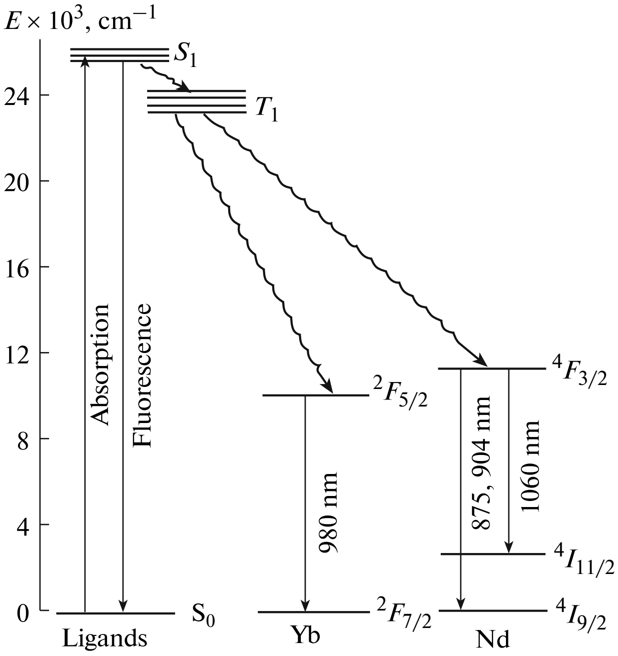


Fig. 1. Energy level diagram for triplet states of ligands and emitting levels of Nd(III) and Yb(IIII).

The reagents under consideration form with lanthanide(III) ions complexes insoluble in water and soluble in organic solvents; therefore, there are two ways to observe their luminescence: in extracts and in suspensions of precipitates in water–organic solvent solutions [5]. The latter variant was used in this work. The water : organic solvent ratio was 9 : 1. At component concentrations used in this study, no precipitation was observed.

Studying the luminescence intensity as a function of the pH of complex solutions showed that maximum Nd(III) and Yb(III) luminescence is observed at pH 7. The ratio of the components in the complexes with anthranyl acids under consideration is Ln : L = 1 : 3. To objectively verify the composition of the complexes, we synthesized and study neodymium homo- and heteroligand complexes with 2-(*N*-amylamino)benzoic acid and phenanthroline as an additional ligand. Elemental analysis and thermogravimetry data confirm the above metal : ligand ratio (1 : 3). The IR spectra of the complexes show easily identified bands of symmetric and asymmetric stretching vibrations of the deprotonated carboxyl group. The differ-

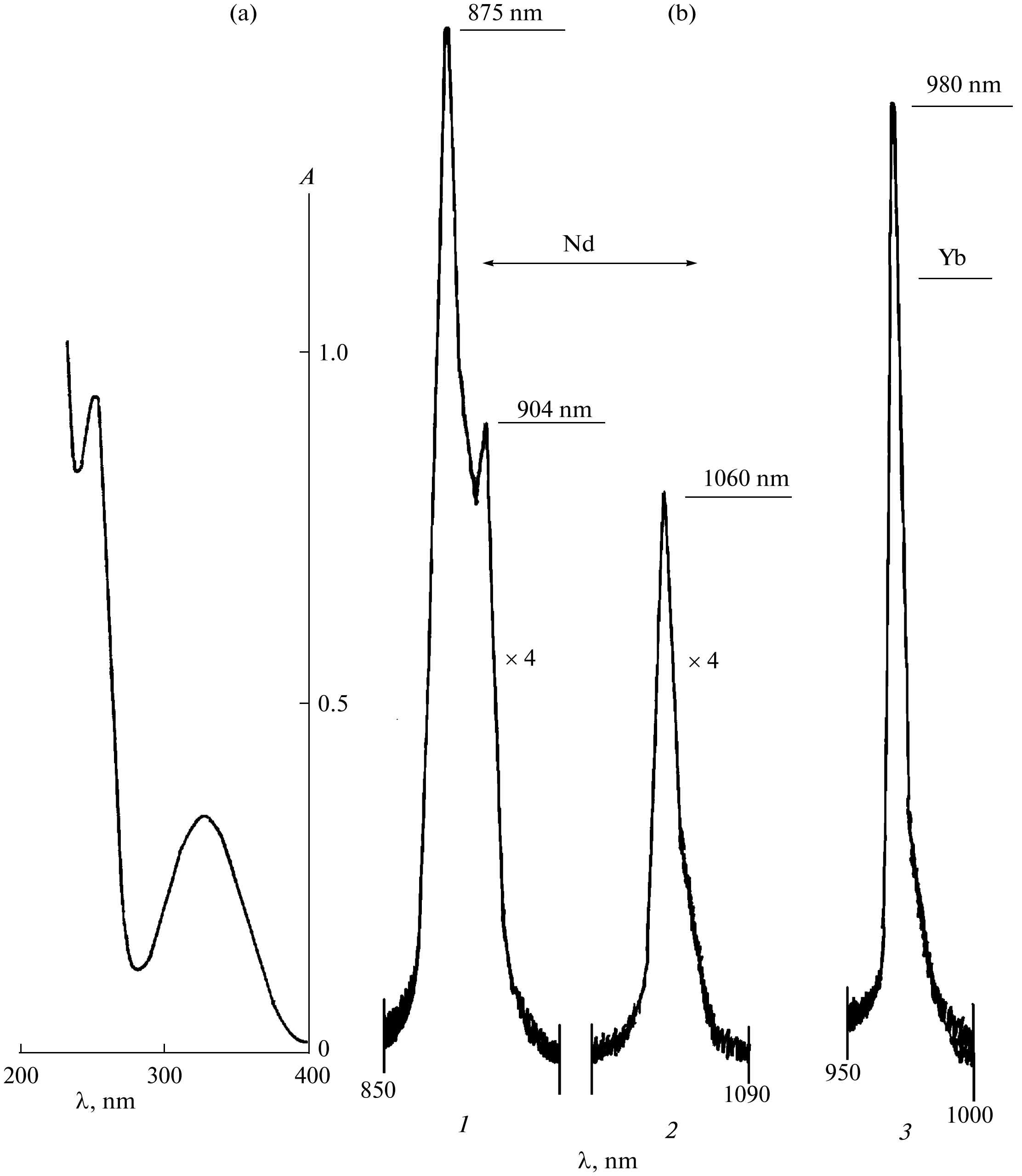


Fig. 2. (a) Absorption spectra of Nd(III) ions and (b) luminescence spectra of (*1*, *2*) Nd(III) and (*3*) Yb(III) in complexes with L4. (a) $c_{\mathrm{Nd}} = 1 \times 10^{-5}$ mol/L, $c_{\mathrm{L4}} = 3 \times 10^{-5}$ mol/L; (b) $c_{\mathrm{Nd,Yb}} = 2 \times 10^{-4}$ mol/L, $c_{\mathrm{L4}} = 2 \times 10^{-3}$ mol/L, pH 7.

ence between the stretching vibration frequencies $\Delta\nu(\mathrm{COO^-}) = \nu_{as} - \nu_s$ is within 190–220 $\mathrm{cm^{-1}}$, so that the carboxyl group can be assigned both the bidentate and bidentate/bridging function.

Inasmuch as the Yb(III) ion has one emitting ($^2F_{5/2}$) and one ground state ($^2F_{7/2}$) levels, the luminescence spectrum of its complexes shows one band with a maximum at 980 nm. The luminescence spectrum of the Nd(III) complexes show two bands arising from transitions from one emitting level ($^4F_{3/2}$) to different ground state sublevels ($^4I_{9/2}$), $^4I_{11/2}$): the first band with maxima at 875 and 904 nm and the second band with a maximum at 1060 nm (Fig. 2b). It is worth noting that the intensity ratio of these bands differs from that in the spectra of the Nd(III) complexes with organic dyes [8] and β-diketones [10] where the band at $\lambda_{\max} = 1060$ nm is the strongest one and, for the first band, the luminescence intensity at 904 nm is higher than that at 875 nm. This can be explained by a different structure of the coordination polyhedron involving the nitrogen atom bound to a hydrocarbon radical of different length.

Table 1. Comparison of the luminescence intensities of the Nd(III) and Yb(III) ions in complexes with N-alkyl-substituted 2-aminobenzoic acids ($c_{\mathrm{Nd,Yb}} = 1 \times 10^{-4}$ mol/L, $c_{\mathrm{L}} = 1 \times 10^{-3}$ mol/L, identical recording conditions)

Ligand	E_{T_1}, cm^{-1}	I_{lum}, arb. units, at λ, nm			
		Nd(III), transition			Yb(III), transition
		$^4F_{3/2} \longrightarrow {}^4I_{9/2}$		$^4F_{3/2} \longrightarrow {}^4I_{11/2}$	$^4F_{5/2} \longrightarrow {}^2F_{7/2}$
		875 nm	904 nm	1060 nm	980 nm
L1	24390	9	7	5	12
L2	23810	17	14	10	25
L3	24210	59	40	47	95
L4	24100	115	70	72	550
L5	23750	101	65	70	505
L6	23360	7	5	3	10

Comparison of data in Table 1 demonstrates that the Yb(III) luminescence intensity (the $^2F_{5/2} \longrightarrow {}^2F_{7/2}$ transition) is two- to fivefold higher than for Nd(III), which has several sublevels of the ground-state level with possible radiation energy losses at them.

As is known, the inner coordination sphere of Ln(III) in complexes with the vast majority of organic ligands contains water molecules, their number mainly depending on the hydrophobic properties of the ligands. In particular, in Ln(III) complexes with β-diketones containing fluoroalkyl substituents ($\mathrm{R_F}$), the Ln(III) luminescence intensity increases as $\mathrm{R_F}$ becomes longer and, hence, the ligands become more hydrophobic [11]. It is likely that the elongation of the hydrocarbon radical at the nitrogen atom in the complexes under consideration has an analogous effect on luminescence intensity. Figure 3 shows how the Nd(III) and Yb(III) luminescence intensity changes as a function of the length of the hydrocarbon radical at the nitrogen atom. A smooth increase in the luminescence intensity in the series of complexes with L1—L3 followed by a sharp increase for the complexes with L4 and an insignificant decrease in going to L5 is most pronounced for the Yb(III) complexes.

To decrease the quenching effect of water molecules (OH oscillators) on the Ln(III) luminescence, an additional ligand or organic solvents are introduced. They are coordinated to the central ion, thus displacing water molecules from the inner coordination sphere of a complex. Table 2 summarizes the results of studying the effect of additional ligands on the luminescence of the Nd(III) and Yb(III) complexes with N-alkyl-substituted 2-aminobenzoic acids. As is seen, the introduction of Phen, bathoPhen, and TOPO leads to the largest luminescence enhancement. By the degree of Nd(III) and Yb(III) luminescence enhancement, the additional ligands are arranged in the series Phen > TOPO > bathoPhen > DAPM > DAM > DAPhM and Phen > bathoPhen > DAPM > DAM > DAPhM, TOPO, respectively. The introduction of an additional ligand does not change the spectral pattern of the complexes and positions of luminescence maxima.

The introduction of 40 vol % of organic solvents (ethanol, dioxane, acetonitrile, DMSO) into solutions of the complexes leads to a decrease in the Nd(III) and Yb(III) luminescence intensity, which is caused by the destruction of complex suspensions where intermolecular energy losses due to thermal collision are most pronounced.

The introduction of cationic (CTA, CPB, ethonium) and nonionic (Triton X-100 and Tween 80) surfactants in concentrations below the CMC into solutions of the complexes somewhat increases the Nd(III) and Yb(III) luminescence intensity. The other surfactants either have no effect on the luminescence intensity or quench it. Such an effect of surfactants can be caused by a rather strong hydrophobic character of the ligands per se, which in enhanced with an increase in the length of the hydrocarbon radical at the nitrogen atom.

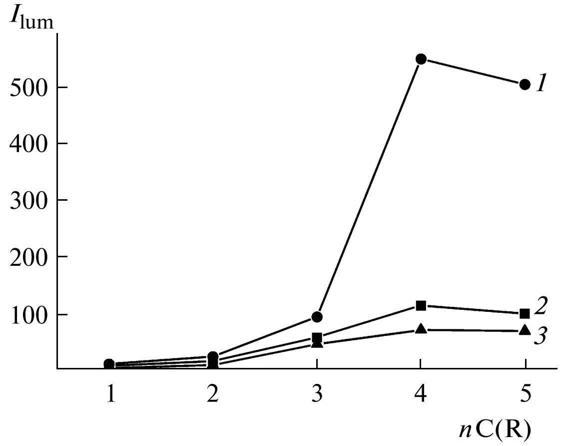


Fig. 3. Luminescence intensity of (*1*) Yb(III) (λ = 980 nm) and (*2, 3*) Nd(III) (λ = (*2*) 875 and (*3*) 1060 nm) as a function of the length of the hydrocarbon radical at the nitrogen atom.

Table 2. Change in the luminescence intensity of Nd(III) and Yb(III) in complexes with L5 upon the introduction of an additional ligand ($c_{\mathrm{Nd, Yb}} = 2 \times 10^{-5}$ mol/L, $c_{\mathrm{L5}} = 2 \times 10^{-4}$ mol/L, $c_{\mathrm{L}} = 2 \times 10^{-4}$ mol/L, pH 7)

Additional ligand	I_{lum}, arb. units			Increase in I_{lum} by n times		
	Nd(III)		Yb(III)	Nd(III)		Yb(III)
	875	1060	980	875	1060	980
–	8	6	5	–	–	–
1,10-Phen	50	25	173	6.3	4.2	34.6
bathoPhen	49	19	88	6.1	3.2	17.8
DAM	6	5	45	0.8	0.8	9.0
DAPM	7	5	60	0.9	0.8	12.0
DAPhM	7	3	12	0.9	0.5	2.4
TOPO	58	29	120	7.3	4.8	24

Thus, our findings demonstrate that the Yb(III) luminescence is almost an order of magnitude stronger than the Nd(III) luminescence. The luminescence intensity can be increased several-fold by introducing an additional ligand, which leads to the formation of a heteroligand complex.

REFERENCES

1. F. Marchetti, C. Pettinari, and R. Pettinari, Coord. Chem. Rev. **249**, 2909 (2005).
2. J.-C. G. Bünzli and C. Piguet, Chem. Soc. Rev. **34**, 1048 (2005).
3. S. Tanabe, C.R. Chim. **5**, 815 (2002).
4. M. A. Katkova, A. G. Vitukhnovskii, and M. N. Bochkareva, Usp. Khim. **74** (12), 1193 (2005).
5. N. S. Poluektov, L. I. Kononenko, N. P. Efryushina, and S. V. Bel'tyukova, *Spectrophotometric and Luminescence Methods of Lanthanide Determination* (Naukova Dumka, Kiev, 1989) [in Russian].
6. Z. M. Topilova, S. B. Meshkova, D. V. Bol'shoi, et al., Zh. Neorg. Khim. **42** (1), 99 (1997) [Russ. J. Inorg. Chem. **42** (1), 92 (1997)].
7. A. O'Riordan, E. O. Connor, S. Moynihan, et al., Thin Solid Films **497**, 299 (2006).
8. N. V. Rusakova and S. B. Meshkova, Zh. Anal. Khim. **45** (10), 1914 (1990).
9. M. Tsvirko, Yu. Korovin, and N. Rusakova, J. Phys.: Conf. Series **79**, 012025 (2007).
10. Org. Synth. **79**, 196 (2002).
11. S. B. Meshkova, N. V. Rusakova, Z. M. Topilova, et al., Koord. Khim. **18** (2), 210 (1992).