Russian Chemical Bulletin, International Edition, Vol. 51, No. 12, pp. 2303—2305, December, 2002

Luminescence of lanthanides in complexes with chromophoric crown ethers

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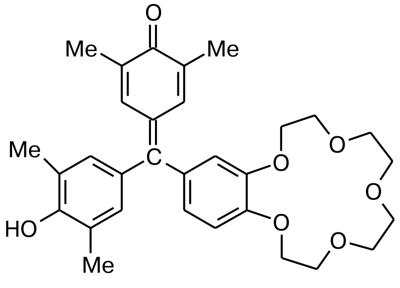
Spectral luminescence characteristics, *viz.*, quantum yields and luminescence lifetime, of the Yb^{3+} and Nd^{3+} ions in aqueous-methanolic solutions of their complexes with chromophoric benzo-15-crown-5 derivatives were determined. The efficient 4f-luminescence (λ_{exc} = 337 nm) is due to the intramolecular transfer of the excitation energy from the chromophoric moiety of the molecule to the Ln^{3+} ion.

Key words: IR luminescence, ytterbium, neodymium, complexes, crown ethers.

Among all lanthanide ions (Ln^{3+}), manifesting 4f-luminescence, only some of them, in particular, Yb^{3+} (λ_{max} = 980 nm) and Nd^{3+} (λ_{max} = 880, 1060, and 1340 nm), are characterized by luminescence in complexes with organic ligands, which absorb the light predominantly in the visible spectral region. This is attributed to the fact that long-lived triplet (T) levels of the most part of colored reagents have a higher energy than low-lying radiative levels of these ions ($^2F_{5/2}$ is 10200 cm^{-1} for Yb^{3+}, and $^4F_{3/2}$ is 11500 cm^{-1} for Nd^{3+}). However, the 4f-luminescence from these levels is quenched due to high-frequency (3500 cm^{-1}) vibrations of the OH groups of the solvent molecules, which enter the coordination sphere of the complexes. As a consequence, they exhibit fairly low luminescence characteristics of Ln^{3+}.[1] This disadvantage can be eliminated, to a great extent, in the case of ligands, which shield, on the one hand, the complex-forming ion from the quenching effect of the solvent molecules and, on the other hand, favor the efficient transfer of the excitation energy to the Ln^{3+} ion.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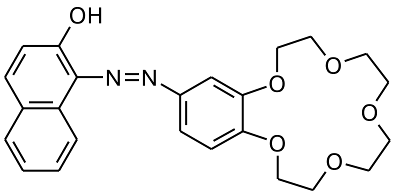
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In this work, we studied the IR luminescence of the Yb^{3+} and Nd^{3+} complexes with chromophoric crown ethers **1** and **2**, *viz.*, ligands satisfying, to a great extent, the above requirements.

Experimental

The initial ytterbium and neodymium nitrates were prepared as hexahydrates by the dissolution of weighted samples of the oxides (99.98% purity) in HNO_3 followed by evaporation. Ligands **1** and **2** were synthesized from 4´-formylbenzo-15-crown-5 (IBC Advanced Technologies, USA) and 2,6-dimethylphenol in the presence of TsOH and from 4´-aminobenzo-15-crown-5 (IBC Advanced Technologies, USA) and 2-naphthol, respectively, using a known procedure.[2] Ligand **1**. Found (%): C, 71.51; H, 6.98. $C_{31}H_{36}O_7$. Calculated (%): C, 71.40; H, 7.09. Ligand **2**. Found (%): C, 65.73; H, 5.99; N, 6.39. $C_{24}H_{26}N_2O_6$. Found (%): C, 65.61; H, 6.08; N, 6.49. The characteristics of the synthesized compounds coincided with the published data. The lanthanide complexes were prepared by the interaction of equimolar amounts of their hexahydrate nitrates and methanolic solutions of **1** and **2** in the presence of triethyl orthoformate as described previously.[3] All complexes were isolated in the solid state and characterized by luminescence, IR and UV spectroscopy.

IR spectra were recorded on an IR-75 spectrometer in pellets with KBr. UV spectra were recorded on a Specord UV-Vis spectrometer in MeOH. The luminescence and luminescence excitation spectra were obtained on an SDL-1 spectrometer with FEU-62 and FEU-79 photoelectron multipliers at 298 K. All spectra were corrected with account for the spectral sensitivity of the FEU. A DKsSh-150 lamp was the source of spectral excitation. The positions of the T levels of the ligands were

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2138—2140, December, 2002.

1066-5285/02/5112-2303 $27.00 © 2002 Plenum Publishing Corporation

determined from the low-temperature phosphorescence spectra of the gadolimium complexes with these ligands. The relative quantum yields of 4f-luminescence (ϕ) of the Yb^{3+} and Nd^{3+} ions in the complexes (solution of Zn tetraphenylporphyrin, whose quantum yield is 0.03, was a reference) and the luminescence lifetime (τ) (an LGI-21 N_2 laser was the excitation source, λ_{max} = 337 nm, pulse duration 15 ns) were determined using a published procedure.[4]

Results and Discussion

The complexes under study are stable for several days in methanolic solutions at room temperature, which is supported by the absence of changes in the absorption spectra (Fig. 1, *a*). Almost complete coincidence of the 4f-luminescence excitation spectra for the Yb^{3+} and Nd^{3+} complexes in combination with the absorption spectra indicates that the excitation energy is transferred from the organic moiety of the complex molecule (energies of the T levels are equal to 15850 and 16270 cm^{-1} for ligands **1** and **2**, respectively) to the radiative levels of the lanthanides due to the intramolecular character of transfer.

All complexes studied exhibit the 4f-luminescence of the Yb^{3+} and Nd^{3+} ions (Fig. 1, *b*), decaying according to the exponential law. Some characteristics of luminescence are presented in Table 1. As should be expected for the complexes with the same ligands, for the Yb complexes the quantum yield and lifetime of luminescence are higher and, in addition, comparable with those for the ytterbium and neodymium complexes with other macrocyclic ligands.[5] The molecular luminescence of the ligands (λ_{exc} = 313 nm) characterized by a broad diffuse band in a region of 475—560 nm (**1**) and 490—555 nm (**2**) is almost completely quenched in the complexes. This can indicate the efficiency of the intramolecular transfer of the excitation energy.[6]

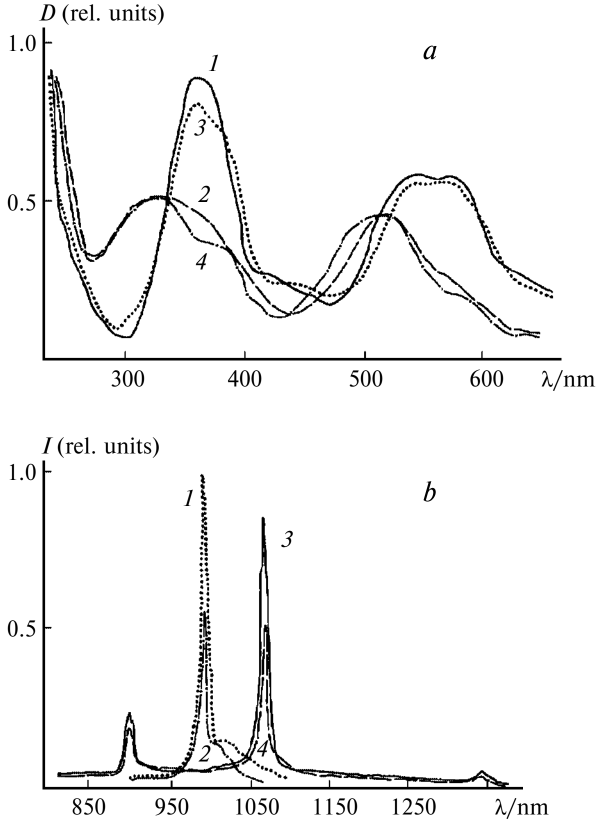

Fig. 1. Absorption (*a*) and 4f-luminescence (*b*) spectra of Yb—**1** (*1*), Yb—**2** (*2*), Nd—**1** (*3*), and Nd—**2** (*4*) in MeOH at 298 K, $5.0 \cdot 10^{-5}$ mol L^{-1}.

Table 1. Luminescence characteristics of the ytterbium and neodymium complexes with chromophoric crown ethers **1** and **2**

Complex	$\phi \cdot 10^3$ *	τ/μs*
Yb—**1**	8.8	4.2
Yb—**2**	6.6	3.8
Nd—**1**	1.2	0.9
Nd—**2**	0.9	0.8

* The error of measurement was ±10%.

The complex formation of lanthanide nitrates with ligand **1** produces complexes with the metal to ligand ratio equal to 1 : 1, which is confirmed by elemental analysis data and characteristic changes in the IR spectra. The latter are almost identical to those for the complexes with benzo-15-crown-5.[7] This suggests the coordination of the Ln^{3+} ions to five O atoms of the macrocycle and O atoms of two bidentate NO_3^- groups. It should especially be emphasized that the IR spectra of the complexes with ligand **1** has no absorption in the region from 3350 to 3300 cm^{-1} characteristic of water molecules in the internal coordination sphere. Therefore, the coordination number of ytterbium and neodymium is nine.

In the case of ligand **2**, the 1 : 1 complexes were also isolated. It could be expected that, in addition to the crown ether cavity, one more lanthanide ion coordinates to the O atoms of the naphthol group and to the N atom of the diazo group. However, by analogy to the lanthanide-1-(pyridyl-2′-azo)naphthol-2 complex, such a coordination can occur only at pH >6.[8]

Taking into account that the Yb^{3+} and Nd^{3+} ions in the complexes with benzo-15-crown do not virtually luminesce and the efficiency of their 4f-luminescence is low[9] in the complexes with sulfophenyl complexones (Phthalexone S, Xylenol Orange) and diazo dyes with the six-membered heterocycle (1-(pyridyl-2′-azo)-naphthol-2, 1-(thiazolyl-2′-azo)naphthol-2), one can suggest that the molecules of ligands **1** and **2** perform a dual function: (1) aromatic fragments are so-called "photoantennas," *i.e.*, accumulators of the excitation energy[10]; (2) crown moiety shields the complex-forming ion from vibrations of O—H of the solvent molecule. We found a similar effect for the luminescence of ytterbium cryptates.[11]

Thus, main requirements to the ligands, whose complexes could provide an efficient luminescence of the Ln^{3+} ions in the near-IR spectral region, are the following: (1) highly dentate character (O,N-donor atoms), (2) chromophoric groups ("photoantennas"), and (3) certain energy of the T levels (at least 13500—14000 cm^{-1}).

This work was financially supported by the National Academy of Sciences of Ukraine (Project No. 249/2001).

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Received January 30, 2002;
in revised form June 28, 2002