Complexes of lanthanide ions with dibenzodioxatetraazamacrocyclic ligands

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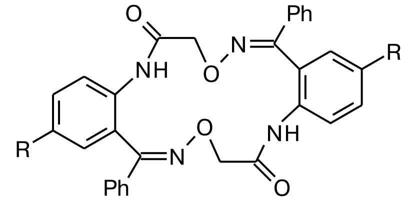
Efficiency of luminescence of europium and ytterbium ions in complexes with three 16-membered dibenzodioxatetraazamacrocycles was estimated.

Key words: luminescence, europium, ytterbium, complexes, tetraazamacrocycles.

Researchers are interested in luminescence properties of lanthanide ions because of their high potential as labels and probes for biochemical and biomedical use.[1] Special attention is given to lanthanide complexes with biologically active organic ligands, such as dibenzomacroheterocycles with antiaggregation activity.[2] In this work, we studied the spectral luminescence properties of europium and ytterbium ions in complexes with 8,18-disubstituted 6,16-diphenyl-1,2,3,11,12,13-hexahydrodibenzo[*g*,*o*]-4,14-dioxa[1,5,11,15]tetraazacyclohexadecyne-2,12-diones (L^1—L^3). Their syntheses have been described by us previously.[2]



R = Me (L^1), Cl (L^2), Br (L^3)

These lanthanides were chosen because, on the one hand, the luminescence of europium(III) is commonly used in biomedical practice. On the other hand, although lanthanide ions (especially Yb^{3+}) emitting in the near-IR spectral region were not used in immunofluorescence analysis up to now, they seem promising, because biological objects have no background emission in this region.

Experimental

Synthesis of YbL^2 complexes. Ytterbium nitrate hexahydrate (0.027 g, 0.058 mmol) was added to a suspension of macrocycle L^2 (0.03 g, 0.0523 mmol) in MeCN (25 mL). The mixture was refluxed for 24 h and concentrated on a rotary evaporator. The dry residue was crystallized from MeCN. The yield of the YbL^2 complex was 0.045 g (83%).

Table 1. Physicochemical characteristics of the Eu(Yb)L^{1-3} complexes

Complex	Yield (%)	Found/Calculated (%) C	H	N	Molecular formula
EuL^1	95	42.45	3.54	10.81	$C_{32}H_{32}EuN_7O_{15}$
		42.39	3.56	10.81	
EuL^2	78	38.03	2.75	10.35	$C_{30}H_{26}Cl_2EuN_7O_{15}$
		38.03	2.77	10.35	
EuL^3	84	34.82	2.55	9.43	$C_{30}H_{26}Br_2EuN_7O_{15}$
		34.77	2.53	9.46	
YbL^1	96	41.39	3.47	10.58	$C_{32}H_{32}N_7O_{15}Yb$
		41.43	3.48	10.57	
YbL^2	83	37.21	2.73	10.21	$C_{30}H_{26}Cl_2N_7O_{15}Yb$
		37.20	2.71	10.12	
YbL^3	87	34.05	2.43	9.28	$C_{30}H_{26}Br_2N_7O_{15}Yb$
		34.08	2.48	9.27	

The YbL^1, YbL^3, and EuL$^{1-3}$ complexes were synthesized similarly in high yields (Table 1).

All complexes were characterized by the data of elemental analysis (see Table 1) and luminescence, IR, and UV spectroscopies.

IR spectra were recorded on a Specord IR-75 spectrometer in $CHCl_3$. UV spectra were measured on a Specord M-40 UV—Vis spectrometer in DMF. Luminescence of Eu^{3+} and Yb^{3+} ions in the complexes under study is observed upon UV excitation (Xe-150 xenon lamp; SDL-1 spectrofluorimeter equipped with a system of photon counting and a unit for phosphorimetric measurements). The relative quantum yield of luminescence (ϕ) was determined by a known method[3] using $Ru(bipy)_3$ and Zn tetraphenylporphyrin as standards for Yb^{3+} and Eu^{3+}, respectively. The luminescence lifetime (τ) was found as described previously[4] using an LGI-21 nitrogen laser (pulse duration 8—10 ns, λ = 337 nm). Quantum-chemical calculations were performed by the PM3 semiempirical method using the HyperChem 7 Evaluation program package.

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Results and Discussion

The IR spectra of the L^{1-3} ligands and Eu(Yb)L^{1-3} complexes differ insignificantly, and the frequencies of the ν(NH), ν(C=O), and ν(C=N) stretching vibrations depend very slightly on the nature of the ligand and metal. The spectra of the complexes contain a broad band in a region of 3300—3400 cm^{-1} characteristic of coordinated water molecules. In addition, they contain bands of coordinated nitrate groups with maxima at 810, 1000, 1310, and 1440 cm^{-1}. The intensities of these bands and the difference between the frequencies ($\Delta\nu = 1440 - 1310 = 130$ cm^{-1}) indicate[5] the interaction between the metal atom and O atoms of the bidentate nitrate group. The IR spectra of the complexes contain no absorption band (or its intensity is substantially decreased over that of the starting ligand) at 1100 cm^{-1} corresponding to stretching vibrations of the N—O bond of the oxime moiety of the macrocycle. The absence of this band can be explained by loosening of the N—O bond due to the formation of a hydrogen bond between the "oxime" O atoms of the macrocycle and water molecules in the coordination sphere of the complex. The results agree well with the calculation data. We estimated the donor properties of the atoms forming the contour of the L^3 macrocycle. The partial charges on the N (C=$\underline{N}$—O) and O (N—$\underline{O}$—C, C=$\underline{O}$) atoms were calculated in the framework of the PM3 semiempirical method similarly to that described previously.[6] The calculation showed that the O(4) and O(14) atoms of the oxime moiety of the molecule are most probable donors in the macrocycle contour (Fig. 1), and their charge exceeds that on the N atoms of the azomethine moiety by 4.7 times, as well as the O(2) and O(12) atoms of the carbonyl groups, whose charge (compared to that of the N atoms of the C=N moieties) is increased by 7.9 times. Starting from the available X-ray

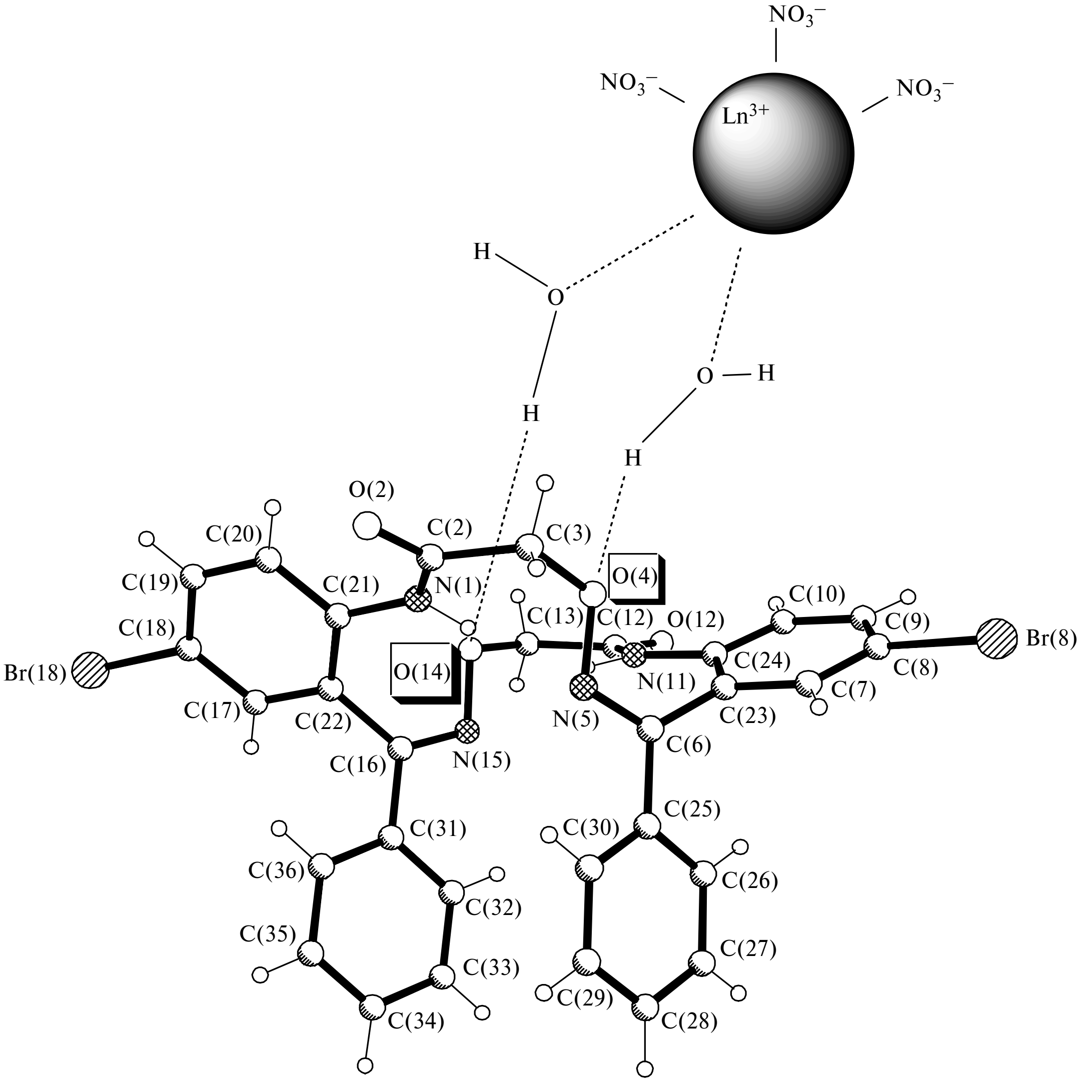

Fig. 1. Proposed structure of the LnL^3 complexes ($Ln^{3+} = Eu^{3+}$, Yb^{3+}).

diffraction data[7] for the L^3 ligand, one can assume that the size of the macrocyclic ligand cavity is insufficient for incorporating europium and ytterbium ions. The O(4) and O(14) atoms of both oxime moieties of the macrocyclic ligand molecule are sterically accessible for bonding with the same lanthanide ion, whereas the arrangement of the O(2) and O(12) atoms of the carbonyl groups does not virtually allow their bonding with the same lanthanide ion to occur. It was found by the fluorescence method[8] that the Ln : L^{1-3} ratio is 1 : 1. The inner coordination sphere of the complexes contains two H_2O molecules, as established by the kinetics of luminescence decay of europium measured as described previously.[9]

It can be assumed that the lanthanide ion in the complexes under study is not bound directly to the macrocyclic ligand. However, the coordination sphere of the complex includes this ion due to H bonds with the coordinated water molecules, *i.e.*, complexes corresponding to the type IV according to the Dalley classification[10] are formed. In these complexes, metal cations are coordinated by their own counterions (in this case, by bidentate nitrate groups) and solvent molecules, which form a system of H bonds with donor atoms of the ligand. Complexes of similar type are described in the literature.[11—14]

Table 2. Data of the optical absorption spectra of the L^{1-3} ligands and EuL^{1-3} complexes in DMF solutions ($5 \cdot 10^{-5}$ mol L^{-1})

Compound	λ/nm	logε
L^1	265.0	4.40
L^2	265.1	4.48
L^3	265.5	4.36
EuL^1	268.9	4.86
EuL^2	265.6	4.75
EuL^3	265.1	4.63

The assumed structure of the inner coordination sphere of the LnL^3 complexes is shown in Fig. 1.

Comparison of the UV spectra of the L^{1-3} ligands and EuL^{1-3} complexes indicates that the absorption bands in the spectra of the latter undergo the minimum (1.5—2.0 nm) bathochromic shift and their intensity increases insignificantly (by 6—8%) (Table 2). The general character of the luminescence spectra (ratio of intensities of bands and their splitting) with maxima at 580, 595, 619, 645, and 694 nm for europium and 980 nm for ytterbium retains in the series of the complexes under study (Fig. 2). It has been found that the quantum yields φ for all complexes increases in organic solvents (DMSO, DMF, acetone, dioxane) in parallel with an increase in

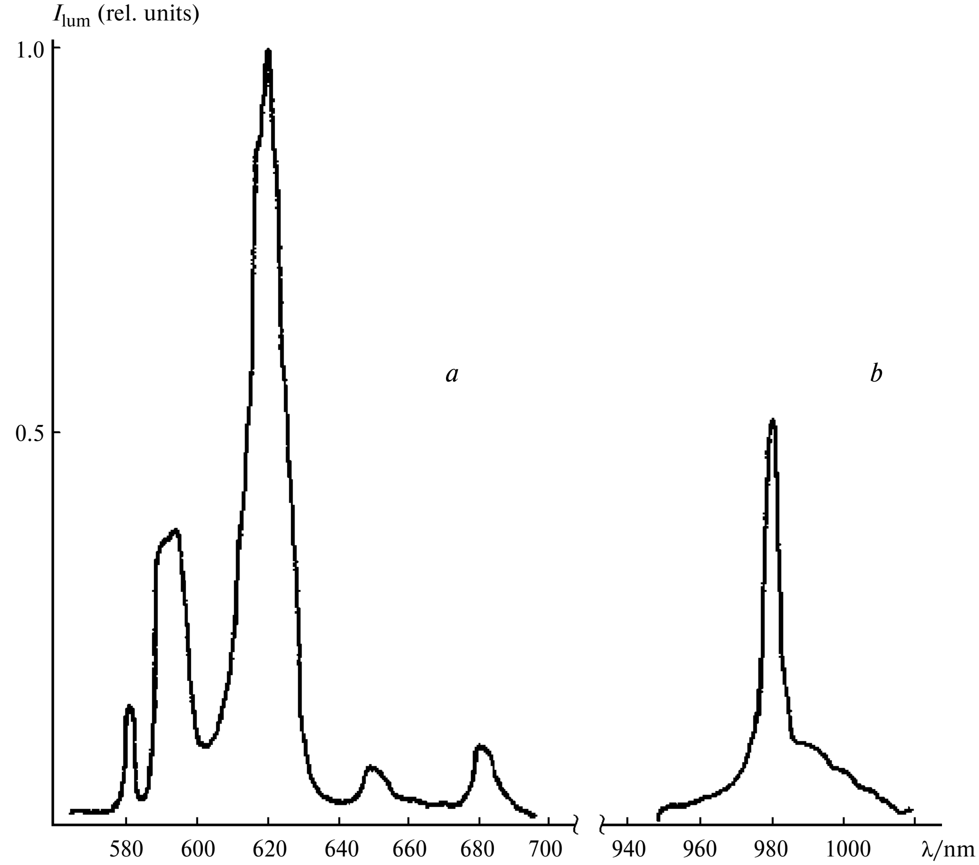

Fig. 2. Luminescence spectra of EuL^2 (*a*) and YbL^2 (*b*) in DMF at 298 K, λ_{exc} = 290 nm.

Table 3. Spectral luminescence properties of the Eu(Yb)L^{1-3} complexes in DMF solutions ($5 \cdot 10^{-5}$ mol L^{-1})*

Complex	$\phi \cdot 10^3$	τ/μs
EuL^1	1.4	175
EuL^2	3.7	490
EuL^3	1.8	232
YbL^1	0.07	0.2
YbL^2	0.41	1.1
YbL^3	0.09	0.4

* The measurement error of the luminescence yield is ±20%, and that of the lifetime is ±10%.

their donor number and dielectric constant. It is rather difficult to elucidate a reason for lower luminescence characteristics of the Eu(Yb)L^1 complexes (Table 3). The lower ϕ and τ values for the Eu(Yb)L^2 and Eu(Yb)L^3 complexes are related, most likely, to the manifestation of the effect of "internal heavy atom" resulting in a change in the energy of excitation to the triplet state of the complex.[15] This effect was observed for other luminescent lanthanide complexes.[9,16] Rather low ϕ and τ values indicate that the excitation energy transfer from the triplet levels of the ligands in a region of 21250—21800 cm^{-1} to the resonance levels of the Eu^{3+} and Yb^{3+} ions is inefficient. This conclusion is confirmed by a difference between the optical absorption spectra of the complexes, where the broad diffuse band with a maximum at 283—291 nm predominates, and the luminescence excitation spectra with prevailing narrow discrete bands corresponding to the intraconfigurational f—f-transitions. These data agree with the above consideration about the character of the metal—ligand bond in the complexes under study. Note that the luminescence of Yb^{3+} ions has been observed for the first time in complexes of this type, and, hence, it requires further studies in more detail.

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