

STRUCTURE AND SPECTRAL-LUMINESCENT PROPERTIES OF LANTHANIDE-CONTAINING COMPLEXES WITH AZACROWN CALIXARENES

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Lanthanide complexes with calix[4]arenes lower rim substituted with two azacrown ether fragments are reported. The size of the substituent cavity varied from 4 to 6 heteroatoms. The complexes were analyzed by means of IR, NMR, ESI mass spectroscopy. It is assumed that the coordination of Ln(III) ions occurs through the donor atoms of the lower rim; the counter anion and solvent molecule are also coordinated. Lanthanide-centered characteristic luminescence was observed in Eu(III), Tb(III) and Yb(III) complexes. The most efficient 4*f*-luminescence is observed for terbium-containing complexes with benzo-crown-derived ligands. The pathways of the sensitization of 4*f*-luminescence are discussed.

Keywords: lanthanide complexes, calix[4]arenes, azacrown ethers, luminescence.

INTRODUCTION. Calix[4]arenes can be considered as universal building blocks, as their molecules have a characteristic feature – the presence of two «rims», which can be modified by functional groups of different nature, and a hydrophobic cavity as an additional binding site. The functionalization of the calix[4]arene macrocycle with polydentate substituents purposefully influences the complexing properties, including the possibilities of the preparation of mono- or heteronuclear complexes of various compositions. Particular interest is shown in the design of calix[4]arenes lower rim substituted with crown ether

fragments. Such combination increases the coordination ability of calixarenes, reduces their conformational mobility and can be used for ion and molecular recognition [1–3].

As a rule, lanthanide-calix[4]arene complexes are formed through coordinating groups at the lower rim which is easily achieved by the functionalization of phenolic OH groups. The first structures of mono- and binuclear europium-containing compounds with *p*-*tert*-butyl-calix[4]arene and its derivatives both in solid state and in solutions were reported by J.M. Harrowfield and coworkers in the 1985–1990s [4–6]. In subsequent works, with the

development of synthetic procedures, both the range of functionalized ligands and the number of lanthanide ions were increased. The general method of synthesis consists in the interaction of lanthanide salts (most often chlorides, nitrates, or picrates) and calix[4]arenes in an anhydrous solvent or in a mixture of solvents in the presence of triethylamine. The latter, as in the case of other metals, promotes the dissociation of phenolic groups, thereby facilitating the formation of complexes.

4f-Luminescence in lanthanide complexes with a number of calix[4]arenes is caused by intramolecular energy transfer from the organic part of the molecule to the metal ion. It can be assumed that it manifests itself in such compounds as crown-calix[4]arenes, while the lanthanide ion can be coordinated by both calix[4]arene and crown ether fragments. The number of studies on the spectral luminescent properties of complexes of such compounds with lanthanide ions is rather low. In the present work, we report our study of the spectral luminescent properties of lanthanide complexes with calix[4]arene derivatives substituted with two azacrown ether fragments. The size of the substituent cavity varied from 4 to 6 heteroatoms.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Calix[4]arenes $L^1H_2 - L^7H_2$ [7, 8] (Table 1) and the corresponding lanthanide-containing complexes were synthesized according to the methods described in [9, 10] in the presence of equimolar quantities of triethylamine. Complexes were isolated in solid state and identified by means of elemental analysis, mass spectrometry, IR, 1H NMR spectroscopy. The geometry optimization of the structures of complexes was performed by the methods of molecular mechanics (HyperChem, MM+).

The absorption spectra in the UV and visible regions were recorded on a spectrophotometer Ulab S261UV in 10 mm quartz cuvettes, and in the IR region ($4000-400\text{ cm}^{-1}$) on a Shimadzu FT-IR8400S spectrophotometer (in KBr pellets).

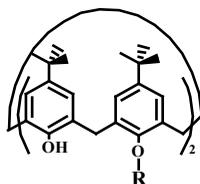
Fluorescence excitation and emission spectra, as well as phosphorescence and 4f-luminescence were recorded on a Fluorolog FL 3-22 spectrofluorimeter (Horiba Jobin Yvon, Xe-450 W ozone-free lamp) equipped with a photomultiplier R928P (Hamamatsu, Japan) for the visible spectral region and a liquid nitrogen cooled InGaAs detector (DSS-IGA020L, Electro-Optical Systems, Inc.) for the NIR.

The values of the singlet (E_s) and triplet levels (E_T) of the derivatives of calix[4]arenes and lutetium-containing complexes were determined by a known procedure [11] at 77K using phosphorescence spectra obtained with different time delays after the excitation pulse ceased. The values of the relative quantum yield of 4f-luminescence (ϕ) of lanthanide ions (measurement error $\pm 20\%$) in complexes were calculated as in [11, 12]. The number of coordinated solvent molecules in complexes was estimated using the Horrocks and Sudnick method [13, 14].

The studied compounds can be divided into two groups. The first consists of calix[4]arene macrocycles linked to azacrown ether by an amide bond ($L^1H_2 - L^4H_2$) and the second consists of their reduced analogs ($L^5H_2 - L^7H_2$). The complexes with the ratio $Ln:L^nH_2 = 1:1$, in which f-cations are coordinated by the donor OH-groups of calix[4]arene, were obtained by the equimolar interaction of the starting materials. Excess of lanthanide salt provides sandwich structures with the 2:1 ratio.

Table 1

Calix[4]arenes modified with azacrown ethers, used in this work.



Ligand	Nomenclature name	R
L ¹ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7-trioxa-10-azacyclododec-10-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene	
L ² H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene	
L ³ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(6,7,9,10,12,13,15,16-octahydro-5,8,14,17-tetraoxa-11-azabenzocyclopentadecen-11-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene	
L ⁴ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7,10,13-pentaoxa-16-azacyclooctadec-16-yl)carbonylmethoxy]-26,28-dihydroxycalix[4]arene	
L ⁵ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7-trioxa-10-azacyclododec-10-yl)ethoxy]-26,28-dihydroxycalix[4]arene	
L ⁶ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)ethoxy]-26,28-dihydroxycalix[4]arene	
L ⁷ H ₂	5,11,17,23-tetra- <i>tert</i> -butyl-25,27-bis[(1,4,7,10,13-pentaoxa-16-azacyclooctadec-16-yl)ethoxy]-26,28-dihydroxycalix[4]arene	

The obtained compounds were analyzed by physico-chemical methods. The ESI mass spectra of all complexes contain peaks of molecular ions corresponding to mononuclear blocks. As an example, Fig. 1 shows a mass spectrum of a lutetium-containing complex with L^2H_2 , which contains the peak of a molecular ion

($m/z = 1414$), which indicates the presence of a chloride anion and one solvent molecule in the complex. The peaks with a lower m/z value correspond to fragments without acetonitrile molecule, chlorine atom, and one or two azacrown ether fragments (peaks with $m/z = 1375$, 1340, 1123, and 906, respectively).

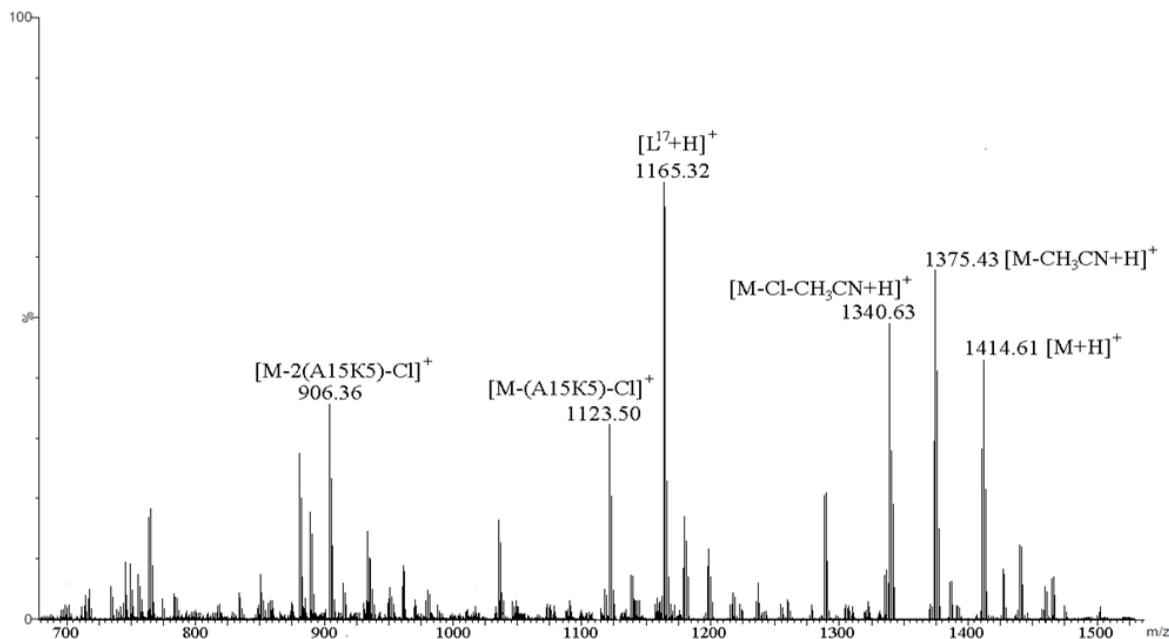


Fig. 1. ESI-mass spectrum of $[LuL^2Cl(CH_3CN)]$.

The coordination of lanthanide ions by the donor groups of calix[4]arene is confirmed by IR spectroscopy data. The vibration band of the OH groups of the starting calix[4]arenes ($\nu(O-H) = 3150-3250\text{ cm}^{-1}$) is absent in the spectra of all complexes. In the spectra of complexes with $L^{1-4}H_2$, the vibration bands of carbonyl groups with maxima in the range of $1640-1690\text{ cm}^{-1}$ undergo a low-frequency shift of $20-30\text{ cm}^{-1}$, which indicates their participation in the coordination of the metal ion. The vibration band of the ether bonds of the lower rim of calix[4]arene ($\nu(C-O) = 1030-1040\text{ cm}^{-1}$)

is shifted to the low-frequency region by $50-60\text{ cm}^{-1}$ in comparison with the spectra of the initial compounds. At the same time, the vibration bands of the ether groups of azacrown substituents ($\nu(C_{\text{crown}}-O) = 1125-1135\text{ cm}^{-1}$) do not change. The formation of complexes is also evidenced by the appearance of a low-frequency band at $450-460\text{ cm}^{-1}$, which refers to the vibrations of lanthanide-oxygen bonds. The position and intensity of the remaining bands in the spectra of complexes do not undergo significant changes in comparison with the spectra of the starting compounds.

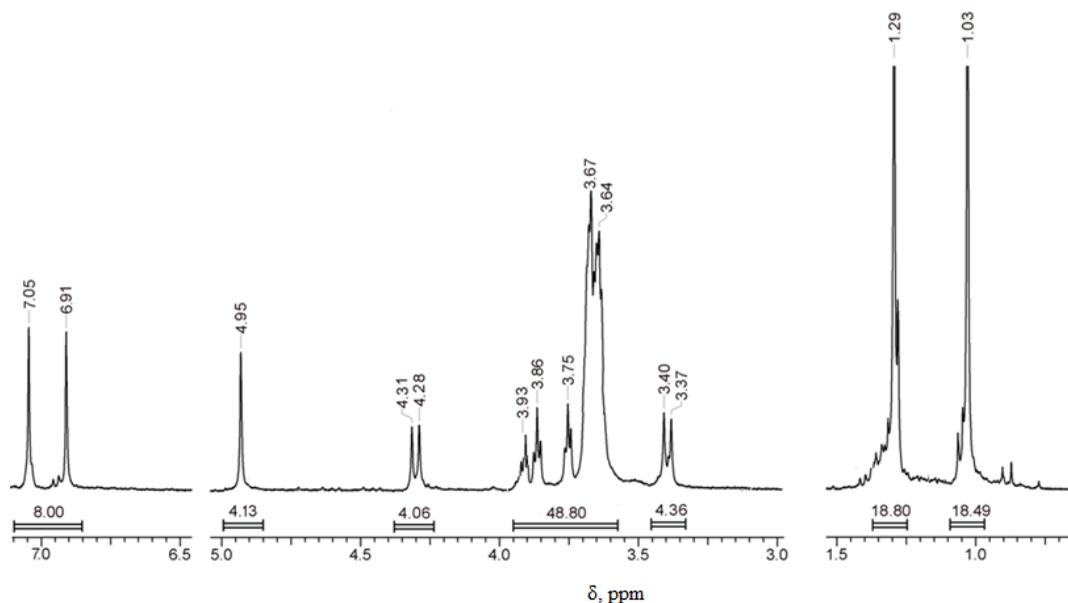


Fig. 2. ^1H NMR spectrum $[\text{LuL}^3\text{Cl}(\text{CH}_3\text{CN})]$ (CDCl_3 , 25°C).

A ^1H NMR spectrum of the $[\text{LuL}^4\text{Cl}(\text{CH}_3\text{CN})]$ complex as an example is shown in Fig. 2. The signals of the protons of phenyl hydroxyl groups, which are at 7.50–7.70 ppm in the spectra of free ligands, disappear upon complexation, which indicates their substitution.

All signals corresponding to the calix[4]arene macrocycle are shifted: the signals of aryl protons and the protons of *tert*-butyl groups are shifted downfield by 0.09–0.11 and 0.05–0.08 ppm, respectively, and the doublets from methylene bridges, which are in the spectra of calixarenes at 3.28 and 4.44 ppm, shift towards each other by 0.09–0.15 ppm, which indicates a smaller flattening of the calix[4]arene conformation in the complex. The participation of the carbonyl oxygen atoms of the amide group in coordination is confirmed by the shift of the $\delta(\text{OCH}_2\text{CO})$ signals of 0.08–0.13 ppm, as well as the appearance of a triplet of N- CH_2 groups at 3.87–3.95 ppm. The position of the signals of the remaining protons of the azacrown ether

substituent in the range 3.60–3.70 ppm does not change. As for amine derivatives (complexes with $\text{L}^5\text{H}_2 - \text{L}^7\text{H}_2$), small changes in the intensity of the main signals of the methylene groups of azacrown ethers in the region of 3.55–4.10 ppm probably indicate the formation of a system of intra- and intermolecular hydrogen bonds.

The data obtained and the MM^+ calculations (Fig. 3) allowed us to conclude that in the complexes with $\text{L}^1\text{H}_2 - \text{L}^4\text{H}_2$ compounds, the coordination polyhedron of lanthanide is formed by four oxygen atoms of the lower rim and carbonyl groups. Considering the coordination of the counterion of lanthanide salt and one solvent molecule (acetonitrile), the coordination number of lanthanide ion in complexes is 8. As for the complexes with calix[4]arenes $\text{L}^5\text{H}_2 - \text{L}^7\text{H}_2$, the coordination site of the lanthanide ion consists of four oxygen atoms of the lower rim of calix[4]arene, the chloride anion, and the solvent molecule, the coordination number of Ln(III) is 6.

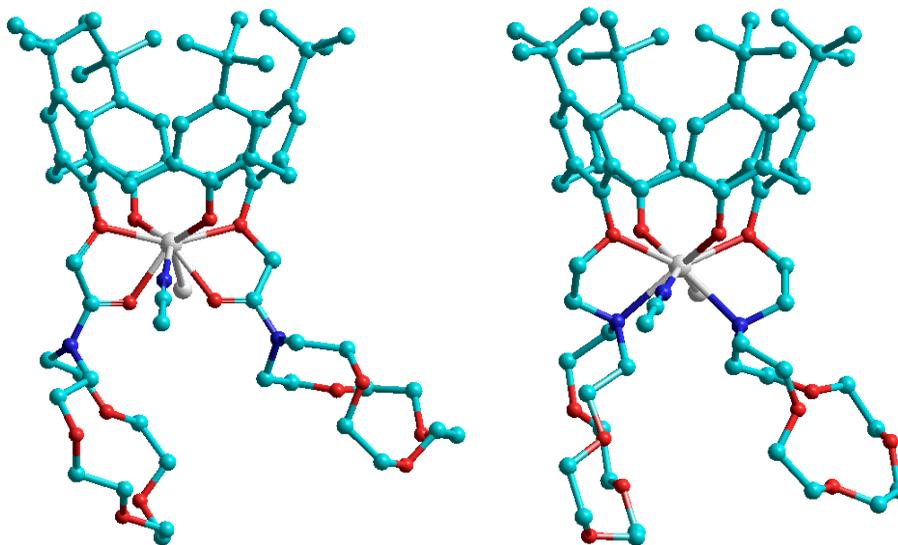


Fig. 3. Calculated spatial models of Ln(III) complexes with L^2H_2 (left) and L^6H_2 (right) (hydrogen atoms are omitted).

The absorption spectra of lanthanide complexes with azacrown ether-functionalized calix[4]arenes are characterized by three bands. The introduction of substituents leads to the appearance of an additional band in the region $\lambda_{\max} = 270\text{--}275$ nm ($37040\text{--}36360$ cm^{-1} , $\log \epsilon = 1.2\text{--}1.5$). Manifesting as a shoulder, it overlaps with the band of the calix[4]arene molecule at $276\text{--}283$ nm ($36230\text{--}35340$ cm^{-1}), and the bands at $284\text{--}291$ nm ($35210\text{--}34360$ cm^{-1}), which correspond to $\pi \rightarrow \pi^*$ transitions in the aromatic fragments of calix[4]arenes. The absorption spectra of the complexes in acetonitrile are also characterized by three bands in the range of $281\text{--}286$ nm ($35590\text{--}34970$ cm^{-1} , $\log \epsilon = 3.78\text{--}3.86$), $290\text{--}294$ nm ($34480\text{--}34000$ cm^{-1} , $\log \epsilon = 3.74\text{--}4.17$) and $304\text{--}310$ nm ($32890\text{--}32260$ cm^{-1} , $\log \epsilon = 3.57\text{--}3.73$). The bathochromic shift of the first two bands is $240\text{--}380$ cm^{-1} compared to ligands, except for the complex with benzo-crown-derivative $[\text{LuL}^3\text{Cl}(\text{CH}_3\text{CN})] - \Delta\lambda = 1260$ cm^{-1}

and 1210 cm^{-1} , for the first and second bands, respectively. The appearance of a band with a maximum in the region of $304\text{--}310$ nm is characteristic of complexes of phenolic calix[4]arenes, when the metal ion replaces protons of OH groups. An increase in the number of glycol fragments in the azacrown ether substituent, as well as the presence of a carbonyl group in the link, practically does not affect the characteristics of the absorption bands of ligands and complexes (Table 2).

One of the conditions for effective $4f$ -luminescence in the coordination compounds of lanthanides is the presence of excited singlet (S_1) and triplet (T_1) levels of ligands higher than the resonance levels of metals. The energy of excited levels was determined by studying the molecular fluorescence and phosphorescence spectra of solutions of the corresponding lutetium complexes (Table 2). The fluorescence spectra of Lu(III) complexes are similar and consist

of a wide band in the range of 390–450 nm with nanosecond range decay time. In comparison with the spectra of free ligands, they are characterized mainly by a bathochromic shift of the fluorescence bands (940–2880 cm⁻¹) and an almost 2.5–3 fold decrease in lif time. The difference is the complexes with 12-azacrown-4-derivatives L¹H₂ and L⁵H₂, where a hypsochromic shift was recorded: 970 cm⁻¹ and 1500 cm⁻¹, respectively, which is probably associated with a deviation of the coplanarity of the complex. Phosphorescence spectra recorded at 77K with a 50 ms time delay are presented as a wide band in the range of 430–470 nm. The energies of triplet

states in lutetium complexes (E_T) were found to be in the range of 21650–22570 cm⁻¹. It should be noted that the energy difference between the S₁- and T₁-levels is small: 570–1300 cm⁻¹, which makes possible energy transfer from the S₁-level of the ligand to the radiative levels of lanthanide ions. The possibility of energy transfer from the S₁-levels to Ln(III) ions does not exclude the participation of T₁-levels in the sensitization of the lanthanide-centered luminescence, as well as energy back transfer from the radiative level of, for example, europium ions (E(⁵D₂) = 21500 cm⁻¹), which is energetically possible [15].

Table 2

Characteristics of absorption, fluorescence and phosphorescence spectra of lutetium complexes with azacrown ether-functionalized calix[4]arenes (C=1×10⁻³ M, CH₃CN).

Complex	$\lambda_I, \lambda_{II}, \lambda_{III}, \text{ nm}$ (log ϵ)			$\lambda_{II}, \text{ nm}$	$\tau, \text{ ns}$	$E_S, \text{ cm}^{-1}$	$\lambda_{\text{phos}}, \text{ nm}$	$E_T, \text{ cm}^{-1}$	$\Delta_{E-T}, \text{ cm}^{-1}$
[LuL ¹ Cl-(CH ₃ CN)]	282 (3.83)	291 (3.82)	305 (3.72)	442	13.4	22620	454	22030	590
[LuL ² Cl-(CH ₃ CN)]	281 (3.84)	291 (3.81)	306 (3.70)	438	13.4	22830	452	22120	710
[LuL ³ Cl-(CH ₃ CN)]	286 (4.28)	294 (4.17)	310 (3.69)	450	18.5	22220	462	21650	570
[LuL ⁴ Cl-(CH ₃ CN)]	284 (3.78)	291 (3.73)	304 (3.57)	441	13.3	22680	457	21880	800
[LuL ⁵ Cl-(CH ₃ CN)]	282 (3.79)	290 (3.74)	306 (3.68)	421	12.7	23750	443	22570	1180
[LuL ⁶ Cl-(CH ₃ CN)]	282 (3.86)	292 (3.81)	307 (3.73)	427	12.1	23420	446	22420	1000
[LuL ⁷ Cl-(CH ₃ CN)]	281 (3.82)	290 (3.77)	305 (3.62)	424	12.8	23590	449	22270	1320

The second, no less important condition for observing intense luminescence is the optimal energy gap between the triplet level of the ligand and the resonance level of the lanthanide ion. As already noted, for each element and each type of ligand, there is a certain optimal energy gap. Thus, for efficient energy transfer in europium complexes, the difference between the energy of the triplet level of the organic ligand and that of the resonant 5D_0 level of europium (III) ion should be between $2500\text{--}3500\text{ cm}^{-1}$ and for terbium (III) ion, $2500\text{--}4000\text{ cm}^{-1}$ [11, 15]. However, for example, for 3-methyl-1-phenyl-4-formyl-5-hydroxypyrazolates of Eu(III) and Tb(III) this regularity, so called «Latva's rule», is not observed, and an intense luminescence of terbium (III) ion is observed at an energy gap of only 200 cm^{-1} , and the europium complex does not exhibit luminescence at $\Delta E = 3450\text{ cm}^{-1}$. In this

case, the luminescence intensity is relatively low due to the scattering of radiation energy at the high-lying sublevels of the ground state [16, 17].

It can be seen from the data obtained that excitation energy transfer from azacrown calix[4]arenes is possible to europium (III) ions (5D_0 and 5D_1 , $E = 17250\text{ cm}^{-1}$ and 19000 cm^{-1} , respectively), terbium (III) ($E(^5D_4) = 20450\text{ cm}^{-1}$), and to the low-lying excited levels of Ln(III) ions luminescent in the NIR region: neodymium (III) ($E(^4F_{3/2}) = 11500\text{ cm}^{-1}$) and ytterbium (III) ($E(^2F_{5/2}) = 10300\text{ cm}^{-1}$).

Nevertheless, in Nd(III) complexes the emission signal is very low, which is probably caused by the quenching effect of C-H- (2950 cm^{-1}) and C-N- (2250 cm^{-1}) vibrations in both the ligand and solvent molecules. In Eu(III), Tb(III), and Yb(III) complexes characteristic 4f-luminescence bands are observed.

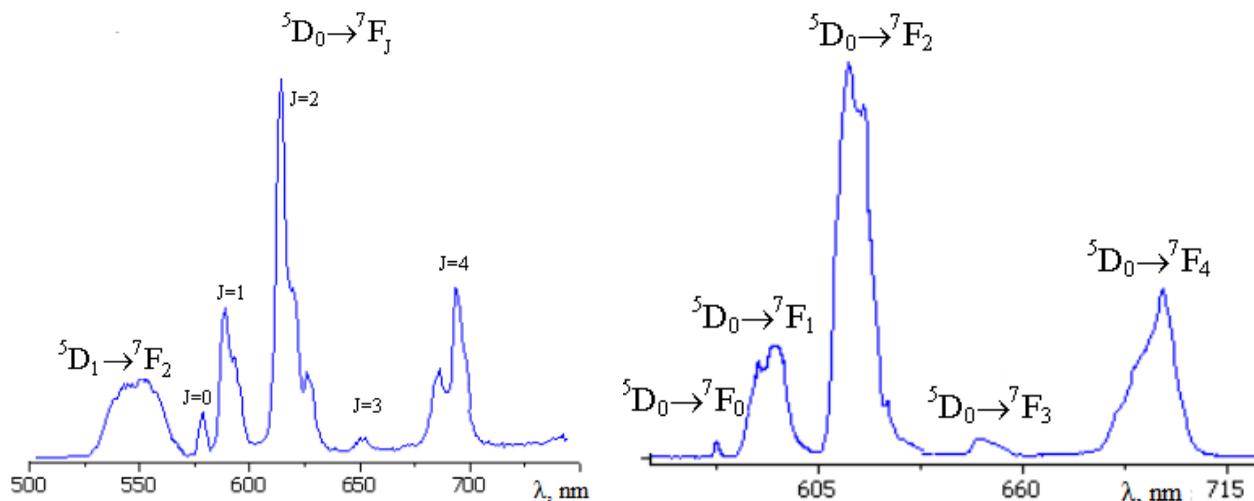


Fig. 4. 4f-Luminescence spectra of complexes $[\text{EuL}^2\text{Cl}(\text{CH}_3\text{CN})]$ (left) and $[\text{EuL}^6\text{Cl}(\text{CH}_3\text{CN})]$ (right).

The coordination environment of the lanthanide ion was analyzed using emission spectra of Eu(III) compounds at 77K [14], whose

luminescence occurred from the 5D_0 and 5D_1 levels. In the spectrum of $[\text{EuL}^2\text{Cl}(\text{CH}_3\text{CN})]$, there is a splitting into three components of

the bands corresponding to the transitions ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$, which is characteristic of eight-coordinated europium ion (Fig. 4). This indicates that the type of the point symmetry group of the polyhedron of the Eu(III) ion is close to C_{2v} and the geometric structure of square antiprism, in accordance with the proposed structural formula. In the spectrum of the $[EuL^6Cl(CH_3CN)]$ complex two intense bands corresponding to the transition from the 5D_0 level to the 7F_2 and 7F_1 levels undergo splitting into two components, which is a consequence of the distortion of the octahedral configuration of europium to C_{4v} type.

The excitation spectra of Tb(III) complexes (Fig. 5) are similar and consist of a wide band with maxima at 363–367 nm. Upon excitation at the maximum of this band, emission spectra are represented as a set of bands of low intensity ligand-centered emission in the 380–420 nm region as well as intense narrow bands of Tb-centered luminescence in the visible region. These peaks correspond to energy transitions: ${}^5D_4 \rightarrow {}^7F_6$ (487 nm), ${}^5D_4 \rightarrow {}^7F_5$ (542 nm), ${}^5D_4 \rightarrow {}^7F_4$ (580 nm and 587 nm), ${}^5D_4 \rightarrow {}^7F_3$ (620 nm), and ${}^5D_4 \rightarrow {}^7F_2$ (643 nm and 650 nm). The quantum yield of terbium complexes is higher than that of the corresponding europium complexes (Table 3).

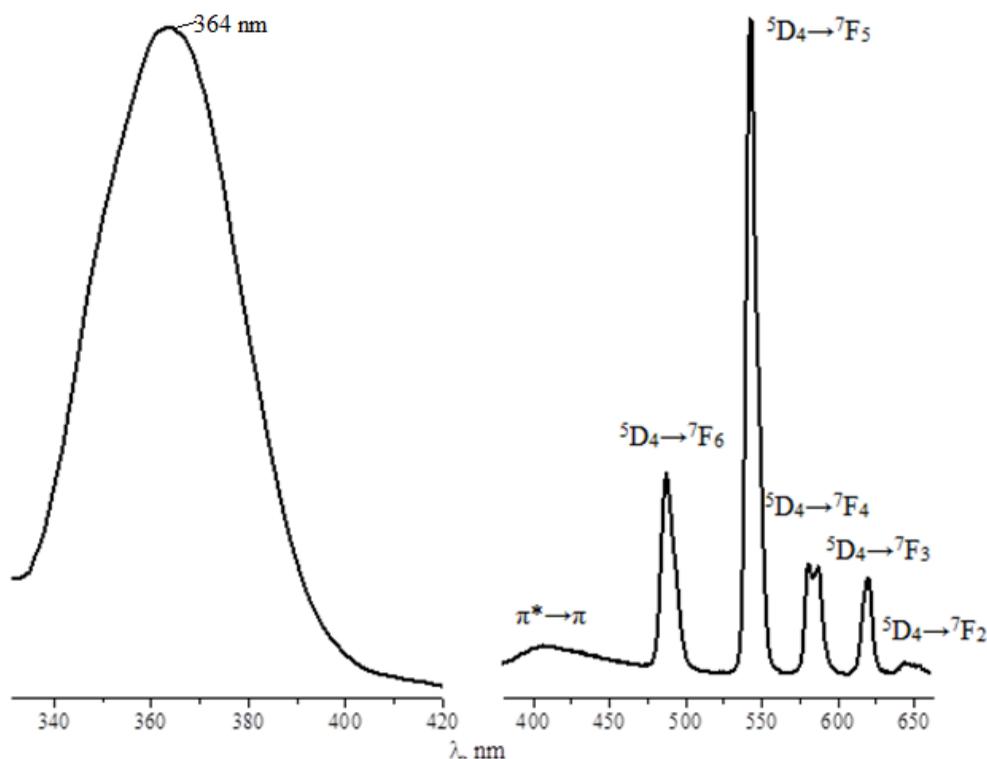


Fig. 5. Photoluminescence excitation (left) and emission (right) spectra of $[TbL^6Cl(CH_3CN)]$.

The highest values of the quantum yields of 4*f*-luminescence are observed for the complexes with the benzo-crown ether derivative L³H₂, as compared to the corresponding complexes [LnL²Cl(CH₃CN)] and [LnL⁶Cl(CH₃CN)] (Table 3). It can be assumed that the presence of a benzene ring in the 15-azacrown-5 heterocycle leads to a redistribution of the electron density not only in the fragments of the substituent,

but also in the molecule of this compound as a whole. This can be caused by an increase in the rigidity of the entire azacrown ether unit and a violation of the symmetry of the arrangement of oxygen atoms in the cycle. The number of coordinated solvent molecules in complexes was estimated and it was found that one solvent molecule is coordinated in all of the complexes.

Table 3

Characteristics of the 4*f*-luminescence of Ln(III) complexes with azacrown ether-calix[4]arenes (C=1×10⁻⁴ M, methanol).

Complex	φ	τ(MeOH), mcs	τ(MeOD), mcs	q(MeOH)
[EuL ¹ Cl(CH ₃ CN)]	0.024	425	507	0.8
[EuL ² Cl(CH ₃ CN)]	0.023	398	469	0.8
[EuL ³ Cl(CH ₃ CN)]	0.032	551	774	1.1
[EuL ⁴ Cl(CH ₃ CN)]	0.019	428	552	1.1
[EuL ⁵ Cl(CH ₃ CN)]	0.024	482	607	0.9
[EuL ⁶ Cl(CH ₃ CN)]	0.017	419	551	1.2
[EuL ⁷ Cl(CH ₃ CN)]	0.020	455	550	0.8
[TbL ¹ Cl(CH ₃ CN)]	0.432	858	2594	0.9
[TbL ² Cl(CH ₃ CN)]	0.448	853	3009	1.2
[TbL ³ Cl(CH ₃ CN)]	0.452	915	3954	1.2
[TbL ⁴ Cl(CH ₃ CN)]	0.421	795	2284	1.1
[TbL ⁵ Cl(CH ₃ CN)]	0.290	871	2712	0.9
[TbL ⁶ Cl(CH ₃ CN)]	0.293	823	2816	1.3
[TbL ⁷ Cl(CH ₃ CN)]	0.386	805	2368	1.1

As can be seen, the optimal gap condition $\Delta E_{T_1} \rightarrow 4f^*$ is not fulfilled for all Ln(III) ions. A particularly large difference between the energy of the triplet levels of the ligands and the energy of the resonant ²F_{5/2} level, which reaches values greater than 10000 cm⁻¹, is observed in the case of ytterbium (III) complexes, which does not allow one to expect intense emission from the complexes. In the luminescence spectrum of the ytterbium complex, one

band is observed due to the transition from the emitting level ²F_{5/2} to the only ground level ²F_{7/2}; however, due to the distortion of the coordination polyhedron, the luminescence band splits with the appearance of three maxima at 982 nm, 1014 nm, and 1060 nm (Fig. 6). As in the case of Eu(III) and Tb(III) complexes, the highest quantum yield of Yb-centered luminescence was found in the complex with the benzo-crown ether derivative L³H₂ (Table 4).

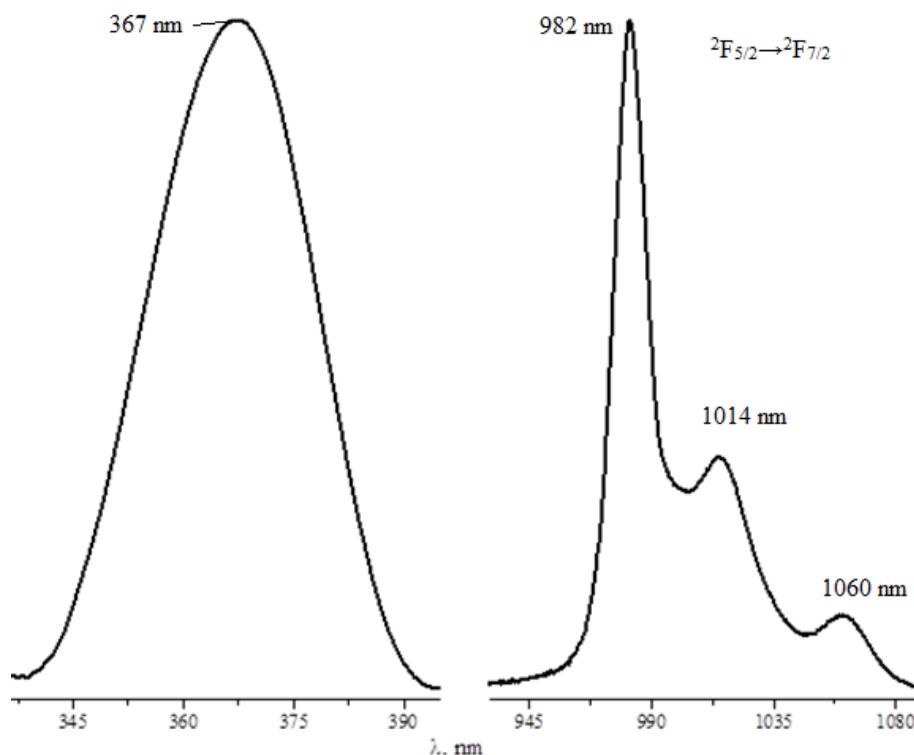


Fig. 6. Photoluminescence excitation (left) and emission (right) spectra of $[\text{YbL}^3\text{Cl}(\text{CH}_3\text{CN})]$.

Table 4

Values of the quantum yield of Yb(III) complexes with azacrown ether-calix[4]arenes.

Ligand	L ¹ H ₂	L ² H ₂	L ³ H ₂	L ⁴ H ₂	L ⁵ H ₂	L ⁶ H ₂	L ⁷ H ₂
φ	0.0042	0.0037	0.0054	0.0032	0.0037	0.0048	0.0041

CONCLUSIONS. Thus, methods of synthesis have been developed and the structure of coordination compounds of lanthanides with lower rim functionalized calix[4]arenes with azacrown ethers has been proposed. It was found that the values of the triplet levels of the ligands facilitate the transfer of excitation energy to the radiative levels of Ln(III) ions, which luminesce both in the visible and in the IR spectral regions. The most efficient 4*f*-luminescence is observed for terbium-containing complexes with benzo-crown-derived ligands.

It was found that the presence of macrocyclic substituents leads to a decrease in the energy of the singlet and triplet levels of calix[4]arenes.



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СТРУКТУРА ТА СПЕКТРАЛЬНО-ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ ЛАНТАНІДВІМІСНИХ КОМПЛЕКСІВ З АЗАКРАУН-КАЛІКСАРЕНАМИ

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Отримано комплекси лантанідів із калікс[4]аренами, заміщеними по нижньому ободу двома азакраун-естерними фрагментами. Розмір порожнини замісника варіювався від 4 до 6 гетероатомів. Комплекси аналізували за допомогою ІЧ, ЯМР, ЕСІ-мас-спектроскопії. Припущено, що координація іонів Ln(III) відбувається за допомогою донорних атомів нижнього ободу, протион і молекула розчинника також є координованими. У комплексах Eu(III), Tb(III) та Yb(III) спостерігали лантанід-центровану характерну люмінесценцію. Найбільш ефективна 4f-люмінесценція спостерігається для тербійвмісних комплексів із лігандами, що містять бензокраун-похідні ліганди. Обговорюються шляхи сенсibiliзації 4f-люмінесценції.

Ключові слова: комплекси лантанідів, калікс[4]арени, азакраунестери, люмінесценція.

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