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# PECULIARITIES OF STRUCTURE AND SPECTRAL-LUMINESCENT PROPERTIES OF CARBOXYMETHOXY-SUBSTITUTED CALIX[4]ARENES AND THEIR COMPLEXES WITH LANTHANIDES

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Spectral-luminescent properties of a variety of carboxymethoxy-substituted *p-tert*-butylcalix[4]arenes and their complexes with lanthanides (Nd, Er, Yb) that exhibit the 4f-luminescence in the IR-spectrum region have been investigated. The effect of substitution of hydrogen phenolic atoms by carboxymethoxy groups on the stability and spectral-luminescent characteristics of both the ligands and lanthanide complexes was analyzed.

Keywords: calix[4]arenes, lanthanide-containing complexes, NIR-luminescence.

*INTRODUCTION.* Having a spatially-organized cavity and specific physicochemical properties, calix[4]arenes are compounds, which are increasingly used in guest-host chemistry [1]. The structure of the spatially organized calix[4]arene molecules delineates a hydrophilic (rims) and a hydrophobic (cavity) fragments, and the size and spatial proximity of the functional groups impart a number of significant features to their chemical behavior. The most accessible method for modifying the lower rim is the replacement of the hydrogen atom of the phenol groups, for example, with different numbers of alkylcarboxyl substituents. It is known that the introduction of four carboxyl fragments along the lower rim of the calix [4] arene promotes the formation of more stable lanthanide-containing complexes in comparison with *p-tert*-butylcalix[4]arene [TBC] [2]. However, until now, the study of the effect of sequential introduction of alkylcarboxyl substituents and, consequently, the structure of symmetrically and asymmetrically substituted calix[4]arenes on the physicochemical, in particular, spectral-luminescent properties of ligands and complexes with lanthanides has not been conducted.

The aim of this work was to establish the relationship between the structure of the series of carboxymethoxy-containing calix[4]arenes ($L^1H_4$—$L^4H_4$) and acid-base, complex-forming, spectral-luminescent properties of ligands themselves, as well as their lanthanide-containing complexes.

The analysis of symmetric ($L^2H_4$, $L^4H_4$) and asymmetric ($L^1H_4$, $L^3H_4$) ligands was made and the number of solvent molecules located in the inner coordination sphere of the complexes was calculated.

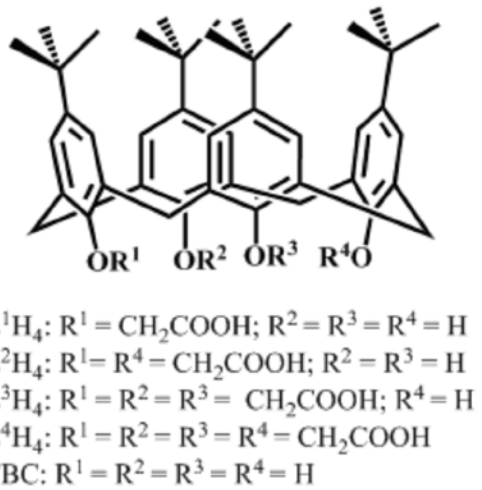

Fig.1. Structure of carboxymethoxy-containing calix[4]arenes $L^1H_4$-$L^4H_4$

*EXPERIMENT AND DISCUSSION OF THE RESULTS*. Ligands $L^1H_4$-$L^4H_4$ and the corresponding lanthanide-containing complexes were synthesized according to the methods described in [2, 3]. Complexes were isolated in solid state and identified by means of elemental analysis, mass spectrometry, IR, 1H NMR spectroscopy (Table S1-S2).

pH-Potentiometric titration was carried out on an ionomer EV-74. The glass electrode SL-43-07 (calibrated with standard buffer solutions) and silver chloride reference electrode were used.

Absorption spectra in the UV and visible regions were recorded on a Specord M-40 UV / VIS spectrophotometer in quartz cuvettes 1-10 mm thick, and in the IR region (4000-400 cm$^{-1}$) on a Shimadzu FT-IR 8400S spectrophotometer (in KBr pellets and in $CHCl_3$).

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

Values of the singlet ($E_S$) and triplet levels ($E_T$) of the derivatives of calyx[4]arenes and lutetium-containing complexes were determined by known procedure [4] at 77K using phosphorescence spectra obtained with different time delays after the excitation pulse.

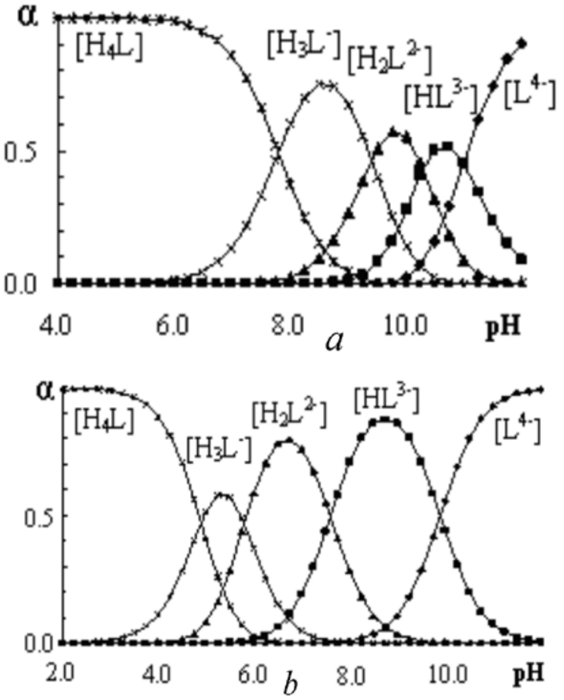

Fig.2. The equilibrium diagrams of protonated ligand forms in water-methanol solutions as a function of pH at 298 K and $\mu$= 0.15 M: a - $L^1H_4$; b - $L^3H_4$

Table 1
**Acid-base dissociation constants of *p-tert*-butyl-calix[4]arenes**

| Compound | $pK_1$ | $pK_2$ | $pK_3$ | $pK_4$ |
|---|---|---|---|---|
| $L^1H_4$ | 7.8 | 9.4 | 10.3 | >11 |
| $L^2H_4$ | 4.3 | 6.8 | 9.6 | >11 |
| $L^3H_4$ | 4.9 | 5.8 | 7.6 | 9.9 |
| $L^4H_4$ | 3.9 | 5.6 | 7.3 | 8.5 |
| TBC [7] | 9.2 | 11.5 | >14 | - |

The integral fluorescence intensity ($I_{fl}$) was measured based on the area under the band contour. The values of the relative quantum yield of 4f-luminescence (φ) of lanthanide ions (measurement error ± 20%) in the complexes were calculated by the methods described in [5, 6].

It is known that one of the characteristic features of calix[4]arenes is the ability to form intramolecular hydrogen bonds, which significantly affect conformational, acid-base, spectral, and complexing properties [7]. The consecutive replacement of OH groups leads to disruption of these bonds, therefore, affects all the above properties, and primarily the dissociation constants of the test compounds (Table 1).

The values of the first dissociation constant of $L^1H_4$ and *p-tert*-butyl-calix[4]arene (TBC) were fairly close, while $pK_1$ value for $L^2H_4$ is lower than for $L^1H_4$ by 3.5. This fact confirms, according to [7], the formation of a cycle of hydrogen bonds involving the COOH group in the case of $L^1H_4$, and a significant weakening of them upon transition to $L^2H_4$. The higher $pK_1$ value in the case of $L^3H_4$ compared to $L^2H_4$ indicates the greater contribution in hydrogen bond formation for $L^3H_4$. Close values of $pK_2$ and $pK_3$ for ligands $L^3H_4$ and $L^4H_4$ indicate the stabilization of the anions $H_3L^-$ and $H_2L^{2-}$ due to the formation of hydrogen bonds by carboxyl groups. The main forms of $L^1H_4$, $L^2H_4$ in the alkaline region are [$H_2L^{2-}$], [$HL^{3-}$], [$L^{4-}$], and the ligands $L^3H_4$, $L^4H_4$ – [$HL^{3-}$], [$L^{4-}$]. The shape of the distribution of ligands $L^1H_4$ and $L^3H_4$ shown in Fig. 2 allows one to consider carboxymethoxy-calix[4]arenes as tetrabasic acids, in which, when complexing, the protons of both carboxyl and phenol groups can be replaced by a lanthanide ion. The results of potentiometric titration point to the weakening of intramolecular hydrogen bonds in the series $L^1H_4 > L^3H_4 > L^2H_4 > L^4H_4$, which is confirmed by the results of 1H NMR and IR spectroscopy.

In $^1H$ NMR spectra of symmetric ligand (TBC, $L^2H_4$, $L^4H_4$) solutions, proton signals of methylene bridges of the calix[4]arene macrocycle appear as two doublets (3.25-3.55 and 4.15-4.55 ppm) with an intensity of 4H for each, and ligands ($L^1H_4$ and $L^3H_4$) - in the form of two pairs of doublets with a small difference in the values of chemical shifts (3.25-3.75 ppm and 4.10-4.25 ppm) with an intensity of 2H for each. It is this type of spectra that is characteristic for “cone” conformation [7]. The broadened singlets from protons of OH groups in weak fields (9.00-10.35 ppm) indicate their participation in the formation of hydrogen bonds. It should be noted that the $\delta_{OH}$ value for the studied ligands changes in such way: TBC (10.34 ppm) > $L^1H_4$ (9.47 ppm) > $L^3H_4$ (9.30 ppm) > $L^2H_4$ (9.00 ppm).

In $^1H$ NMR spectra of complexes with diamagnetic lutetium ion there are no proton signals of the carboxyl and hydroxyl groups, which indicates their replacement by a lanthanide ion and confirms the IR spectroscopy data. The observed decrease in the number of proton signals of *tert*-butyl substituents in the spectra of $LuL^1H$ and $LuL^3H$ complexes indicates, according to [8], the "alignment" of the complex structure compared to the corresponding asymmetrically substituted ligands. The formation of complexes based on symmetrical ligands $L^2H_4$ and $L^4H_4$ does not introduce changes in the number and intensity of the proton signals of these groups, i.e. the symmetry of the coordination center during complexation is preserved. Significant shifts in the signals of protons of aromatic nuclei ($\Delta\delta = +0.12 \pm 0.22$ ppm) and $CH_2CO$-groups ($\Delta\delta = +0.08 \pm 0.14$ ppm) in comparison with ligands $L^1H_4$ - $L^3H_4$ confirm participation of oxygen atoms of ester fragments in coordination of metal in these complexes.

The presence of intense wide bands of stretching vibrations of the OH group in the 3100-3400 $cm^{-1}$ region in IR spectra of $L^1H_4$ - $L^4H_4$ also indicates the presence of intramolecular hydrogen bonds. Replacement of phenol groups with carboxymethoxy ones leads to a shift in the frequency of the bands to the long-wavelength region ($L^1H_4$ (3170 $cm^{-1}$) < $L^2H_4$ (3320 $cm^{-1}$) < $L^3H_4$ (3375 $cm^{-1}$)) as compared to TBC (3130 $cm^{-1}$). These changes in IR spectra, similar to the $^1$H NMR spectra [8, 9], indicate a significant weakening of intramolecular hydrogen bonds with an increase in the number of carboxymethoxy groups.

A significant decrease in the intensities of the stretching vibration bands of OH groups in IR spectra of lanthanide-containing complexes in the region of 3150-3350 $cm^{-1}$, the disappearance of bands in the region ν (C=O) = 1740-1750 $cm^{-1}$, as well as the absorption bands of OH and COOH deformation vibrations in the fingerprints region (730-780, 800-830, 880-910, 1180-1250 $cm^{-1}$) indicate that all the corresponding substituents are connected with the lanthanide ion. This is also confirmed by the appearance of bands in the region of 1595-1600 $cm^{-1}$ and 1440-1470 $cm^{-1}$, related to $\nu_{as}$(C-O) and $\nu_s$(C-O), respectively. It should be noted that, in contrast to $LnL^4H$, a short-wavelength shift (20-50 cm-1) of the ν(-$CH_2$-OAr) oscillations in the 1030-1050 $cm^{-1}$ region is observed for $LnL_1H$ - $LnL_3H$ complexes, confirming the participation of ether oxygen atoms in the complexing of the metal.

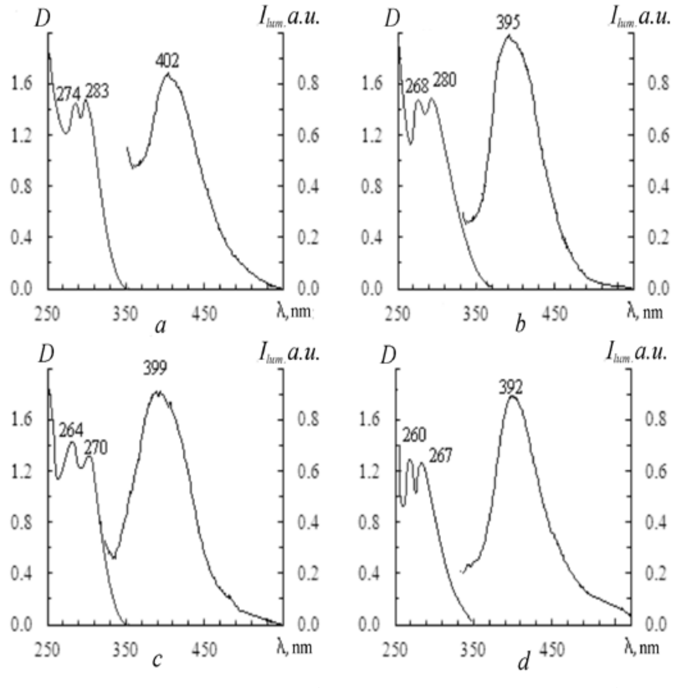

Fig. 3. Absorption and fluorescence spectra of solutions in dioxane at 298 K: a – $L^1H_4$, $\lambda_{exc}$= 308 nm; b – $L^2H_4$, $\lambda_{exc}$= 312 nm; c - $L^3H_4$, $\lambda_{exc}$= 310 nm; d – $L^4H_4$, $\lambda_{exc}$= 309 nm

Table 2.
**Data of the absorption, fluorescence and phosphorescence spectra of calix[4]arenes $L^1H_4$–$L^4H_4$**

| Ligand | Solvent | $\lambda_I$, $\lambda_{II}$ nm (lg ε) | | $\lambda_{fl}$, нм | $\tau_{fl}$, ns | $E_S$, sm$^{-1}$ | $\lambda_{phos}$, nm | $\tau_{phos}$, ms | $E_T$,sm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $L^1H_4$ | DO | 274<br>(3.88) | 283<br>(3.92) | 402 | 9.2±0.2 | 24900 | 420 | 210±8 | 23800 |
| | DMF | 280<br>(3.95) | 286<br>(sh.) | 410 | 9.6±0.2 | 24400 | 429 | 234±8 | 23300 |
| $L^2H_4$ | DO | 268<br>(3.89) | 280<br>(3.93) | 395 | 6.4±0.4 | 25300 | 406 | 208±4 | 24600 |
| | DMF | 288<br>(3.94) | 296<br>(sh.) | 411 | 4.2±0.2<br>15.3±0.5 | 24300 | 422 | 291±4 | 23700 |
| $L^3H_4$ | DO | 264<br>(3.57) | 270<br>(3.50) | 399 | 15.4±0.7 | 25100 | 412 | 259±15 | 24300 |
| | DMF | 278<br>(sh.) | 285<br>(3.70) | 405 | 3.4±0.3<br>13.5±0.8 | 24700 | 436 | 138±9 | 22900 |
| $L^4H_4$ | DO | 260<br>(3.75) | 267<br>(3.78) | 392 | 5.7±0.4 | 25500 | 424 | 140±5 | 23600 |
| | DMF | 278<br>(3.67) | 280<br>(sh.) | 409 | 4.8±0.5<br>18±2 | 24450 | 439 | 280±5 | 22800 |

The absorption spectra of the free ligands in dioxane at room temperature are characterized by wide bands split into two components with maxima at 260-274 nm and 270-283 nm (lgε = 3.50-3.95), which correspond to π→π* -transitions of aromatic fragments (Fig. 3 and Table 1).

It should be noted that as the number of substituents increases, hypsochromic shifts in the absorption band maxima are observed, observed, although the molar extinction coefficients and the intensity ratio of the bands remain constant. In comparison with TBC ($\lambda_I$ = 280, $\lambda_{II}$ = 288 nm), the introduction of one carboxyl group practically does not affect the position and intensity of the absorption bands. When the number of carboxyl (di-, tri- and tetra- substituted ligands) is increased, a hypsochromic shift of the absorption band maxima from 3-6 to 14-16 nm is observed and the absorption intensity decreases by 10-12%. These changes, according to [8], in the absorption spectra in a series of carboxy derivatives of the calix[4]arene are explained by structural changes in the chain of intramolecular hydrogen bonds that form substitutes of the lower rim. A significant difference should be noted in the absorption spectra in the dimethylformamide (DMF) and dioxane (DO) media, which indicates the interaction of ligands with the molecules of the basic solvent - dimethylformamide. Along with the absorption spectra, the fluorescence / phosphorescence spectra of the ligands also undergo significant changes.

Table 3.
**Spectroscopic properties of Lu(III) complexes with $L^1H_4$ – $L^4H_4$ (C=1×$10^{-4}$ M, dioxane)**

| Complex | $\lambda_I$, $\lambda_{II}$, $\lambda_{III}$, nm (lg ε) | | | $\lambda_{fl}$, nm | $\tau_{fl}$, ns | $E_S$,$sm^{-1}$ | $\lambda_{phos}$, nm | $\tau_{phos}$, ms | $E_T$,$sm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $LuL^1H$ | 283<br>(3.74) | 290<br>(3.71) | 307<br>(2.85) | 404 | 6.6±0.3 | 24750 | 424 | 259±9 | 23600 |
| $LuL^2H$ | 273<br>(3.58) | 276<br>(3.59) | 320<br>(2.62) | 406 | 6.0±0.2 | 24600 | 420 | 133±8 | 23800 |
| $LuL^3H$ | 278<br>(3.20) | 284<br>(3.18) | 312<br>(2.36) | 409 | 8.9±0.1 | 24450 | 452 | 344±5 | 22100 |
| $LuL^4H$ | 277<br>(3.90) | 288<br>(sh.) | - | 411 | 9.8±0.2 | 24300 | 445 | 144±5 | 22400 |

Solutions of carboxyalkyl[4]arenes in dioxane show fluorescence in the form of a broad band in the 390-415 nm region (24100-25640 $cm^{-1}$, $\lambda_{exc}$ = 300-320 nm), which corresponds to the transition from the lower excited $^1\pi\pi$ * to the ground level. When a time delay (10-20 μs) and cooling to 77 K were used, the phosphorescence of the ligands was detected, the maximum band of which was batochromically shifted by 15-30 nm relative to the fluorescence (Table 2). The fluorescence spectra of solutions of all ligands in DMF, in comparison with solutions in dioxane, are batochromically shifted by 6-17 nm, and phosphorescence - by 9-24 nm, respectively. The values of the singlet $S_1$ and triplet $T_1$ energy levels, as well as the energy gaps between them, do not undergo significant changes, although for $L^3H_4$ ΔE increases by 960 $cm^{-1}$. Biexponential fitting of the fluorescence decay curves of $L^2H_4$ - $L^4H_4$ in DMF also confirms complexation with solvent molecules. The largest values of τ in comparison with the rest of the series are observed for solutions of $L^3H_4$ in dioxane. The absorption spectra of lanthanide (III) complexes (Er, Yb, Nd, Lu) with identical ligands coincide, indicating that the method of coordination of the lanthanide ion in this row remains the same. The formation of all lanthanide complexes with $L^1H_4$-$L^4H_4$ leads to a bathochromic shift of the maxima of the absorption, fluorescence, and phosphorescence spectra as compared with the ligands (Table 3). The appearance of a broad band in the region of 307-320 nm (lg ε = 2.85-2.36) in the absorption spectra of $L^1H_4$-$L^3H_4$ complexes, according to [10], indicates the participation of phenol OH-groups in complex formation. The stability constants of the corresponding complexes were calculated in anhydrous methanol: (2×$10^{-4}$ M): 8.7 ± 1.6 ($LuL^1H$), 10.3±1.5 ($LuL^2H$), 14.3±0.8 ($LuL^3H$), 18.4±1.4 ($LuL^4H$). As can be seen from the data presented, a significant increase in the stability constants is observed with an increase in the number of carboxymethoxy groups along the lower rim of the ligands.

In all $LnL^1H$ - $LnL_4H$ compounds, 4f-luminescence of $Nd^{3+}$, $Er^{3+}$ and $Yb^{3+}$ ions is realized in the infrared region of the spec-

Table 4

**4f-Luminescent properties of Ln(III) complexes with $L^1H_4$ – $L^4H_4$ (C=1×10$^{-4}$ M, methanol)**

| Complex | λ., nm | φ×10$^3$ | τ ($CH_3OH$), mcs | τ ($CD_3OD$), mcs | *q* |
|---|---|---|---|---|---|
| $YbL^1H$ | 982; 1004; 1052 | 3.7 | 0.62 | 45.2 | 1.4 |
| $YbL^2H$ | 982; 1007; 1050 | 3.2 | 0.55 | 38.4 | 1.6 |
| $YbL^3H$ | 978; 1002; 1026 | 4.0 | 0.71 | 52.3 | 1.2 |
| $YbL^4H$ | 976: 1024; 1051 | 2.2 | 0.41 | 30.1 | 2.2 |
| $NdL^1H$ | 895; 1067; 1075 | 0.23 | 0.07 | 0.42 | 1.2 |
| $NdL^3H$ | 895; 1065; 1076 | 0.18 | 0.05 | 0.32 | 1.8 |
| $NdL^3H$ | 895; 1065; 1075 | 0.29 | 0.09 | 0.54 | 0.8 |
| $NdL^4H$ | 889; 1069; 1073 | 0.15 | 0.04 | 0.30 | 2.4 |
| | | $I_{lum.}$, a.u. | | | |
| $ErL^1H$ | 1530 | 7.8 | | | |
| $ErL^2H$ | 1530 | 5.4 | | | |
| $ErL^3H$ | 1530 | 9.7 | | | |
| $ErL^4H$ | 1530 | 3.6 | | | |

trum. It is known [11] that the efficiency of 4f-luminescence in lanthanide complexes is in definite dependence on the energy of the ligand singlet and triplet levels (Table 3). It was found that the triplet levels of $L^1H_4$ – $L^4H_4$ are higher than the radiating levels of the lanthanide ions, in particular, $Er^{3+}$ ($^4I_{13/2}$, 6500 cm$^{-1}$), $Yb^{3+}$ ($^2F_{5/2}$, 10300 cm$^{-1}$) and $Nd^{3+}$ ($^4F_{3/2}$, 11460 cm$^{-1}$), which make possible an intramolecular energy transfer from the organic part of the complex to the lanthanide ion. The lowest energy (22100 cm$^{-1}$) and the maximum lifetime of the triplet level (344 ms) were registered for the $LuL^3H$ complex. For mono- and di-derivatives, the energy of the triplet levels is practically the same, while the lifetime of the latter is half that of the complex with mono-acid.

The 4f-luminescence of $Er^{3+}$ ions with a maximum at 1530 nm (6540 cm$^{-1}$) corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was observed for the first time in complexes with carboxymethoxy derivatives of calix[4]arenes (Fig. 4). The tendency of the change in the luminescence intensity in complexes with erbium is analogous to changes in the values of the quantum yield of 4f-luminescence in neodymium and ytterbium complexes: $ErL^3H$ > $ErL^1H$ > $ErL^2H$ > $ErL^4H$.

It was determined that the molecular fluorescence of carboxymethoxycalix[4]arenes in complexes with $Nd^{3+}$ is practically quenched in comparison with lutetium-containing complexes, and the 4f-luminescence characteristic of neodymium in the near IR region (850-1100 nm) is observed upon excitation into the ligand absorption band, which indicates the energy transfer from the organic chromophore to the

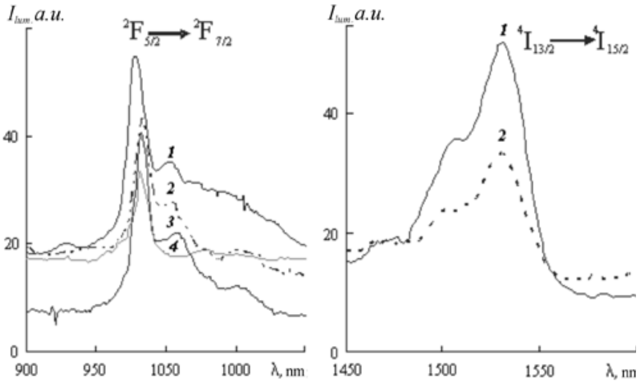

Fig.4. 4f-Luminescence spectra of Yb(III) complexes (a) with $L^3H_4$ (1), $L^1H_4$ (2), $L^2H_4$ (3), $L^4H_4$ (4); Er(III) complexes (b) with $L^3H_4$ (1), $L^4H_4$ (2) ($C=1\times10^{-3}$ M, MeOH, 298 K)

radiating lanthanide ion. Neodymium spectra with ligands $L^1H_4$ - $L^4H_4$ are characterized by bands with a maximum in the range of 889-895 nm (11173 - 11250 cm$^{-1}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition), 1065 - 1069 nm (9350-9400 cm$^{-1}$) and 1073 - 1076 nm (9250 - 9300 cm$^{-1}$), which correspond to the split transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. The relative quantum yields and lifetime of the 4f-luminescence of the complexes in methanol at room temperature are $(0.15\text{-}0.29)\times10^{-3}$ and 0.04-0.09 μs (Table 4). The decay curves of the $Nd^{3+}$ ion luminescence in the studied complexes fit to a single exponential decay law, which indicates the equivalence of the radiating centers.

The positions of the maxima and the structure of the 4f-luminescence spectra of the ytterbium-containing complexes are due to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (975-986 nm) transition and practically coincide for all compounds. At 77 K, the positions of the maxima in these spectra are shifted (by 20-30 cm$^{-1}$) to the long-wavelength region, and the spectra themselves are split into three components. Such a splitting is a consequence of the low symmetry of the coordination polyhedron of these complexes. The splitting of the $^2F_{7/2}$ level is 677, 659, 478, 731 cm$^{-1}$ in complexes with $L^1H_4$ - $L^4H_4$, respectively, that allows us to conclude that the influence of the ligand field of $L^1H_4$ and $L^2H_4$ is the closest to the $Yb^{3+}$ ion. It should be noted that the quantum yield of 4f-luminescence in ytterbium complexes is higher than that for neodymium compounds. Obviously, the determining effect in this case is caused by the vibrations of OH and CH groups of molecules surrounding the lanthanide ion, leading to non-radiative energy losses (Table 4).

The number of methanol molecules (q($CH_3OH$), Table 4) in the inner coordination sphere of $Nd^{3+}$ and $Yb^{3+}$ ions in complexes with $L^1H_4$ - $L^4H_4$ was determined based on the lifetime of 4f-luminescence in $CH_3OH$ and $CD_3OD$ according to [12]. The largest number of solvent molecules is characterized by complexes of $Nd^{3+}$ and $Yb^{3+}$ with tetra- derivative: 2.2 and 2.4, respectively. In complexes with mono- and di-derivatives, the coordination sphere of lanthanide ions contains practically the same number of methanol molecules (1.2-1.8), which indirectly confirms the similarity of coordination nodes of the corresponding complexes. As for complexes with a trisubstituted calix[4]arene, the number of $CH_3OH$ molecules in them is the smallest, which explains the highest values of the quantum yields in a series of these compounds.

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*CONCLUSIONS.* Thus, based on the combination of the results obtained by

means of elemental analysis, mass spectrometry, IR and $^1$H NMR spectroscopy, and taking into account the data of pH-metric titration, spectrophotometric and luminescence measurements, it can be concluded that lanthanide ions form neutral complexes of 1:1 ratio with $L^1H_4$ - $L^4H_4$. This is explained by the presence of mobile hydrogen atoms of phenol and/or carboxyl groups in the molecules of these ligands. An increase in the number of donor substituents leads to changes in the number of solvent molecules in the series $L^3H_4 < L^1H_4 < L^2H_4 < L^4H_4$ from 0.8 to 2.4 for neodymium complexes, from 1.2 to 2.2 - for ytterbium complexes. Both the quantum yield and lifetime of the 4f-luminescence of the neodymium and ytterbium complexes and also the luminescence intensity of the erbium-containing compounds change in the same order.

## ОСОБЛИВОСТІ СТРУКТУРИ ТА СПЕКТРАЛЬНО-ЛЮМІНЕСЦЕНТНИХ ВЛАСТИВОСТЕЙ КАРБОКСИМЕТОКСИЗАМІЩЕНИХ КАЛІКС[4]АРЕНІВ ТА ЇХ КОМПЛЕКСІВ З ЛАНТАНІДАМИ

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Досліджено спектрально-люмінесцентні властивості різних карбоксиметоксизаміщених *п-трет*-бутил-калікс[4]аренів та їх комплексів з лантанідами (Nd, Er, Yb), які виявляють 4f-люмінесценцію в ІЧ-області спектра. Проаналізовано вплив заміщення фенольних атомів водню карбоксиметоксигрупами на стабільність та спектрально-люмінесцентні характеристики як лігандів, так і лантанідних комплексів.

Ключові слова: калікс[4]арени, лантанідвмісні комплекси, люмінесценція у ближній ІЧ-області

## ОСОБЕННОСТИ СТРУКТУРЫ И СПЕКТРАЛЬНО-ЛЮМИНЕСЦЕНТНЫХ СВОЙСТВ КАРБОКСИМЕТОКСИ ЗАМЕЩЕННЫХ КАЛИКС[4]АРЕНОВ И ИХ КОМПЛЕКСОВ С ЛАНТАНИДАМИ

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Исследованы спектрально-люминесцентные свойства различных карбоксиметоксизамещенных *п-трет*-бутил-каликс[4]аренов и их комплексов с лантанидами (Nd, Er, Yb), которые проявляют 4f-люминесценцию в ИК-области спектра. Проанализировано влияние замещения фенольных атомов водорода карбоксиметоксигруппами на стабильность и спектрально-люминесцентные характеристики как лигандов, так и лантанидных комплексов.

Ключевые слова: каликс [4] арены, лантанидные комплексы, люминесценция в ближней ИК-области

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