

Synthesis and characterization of lanthanoid complexes with 3, 3'- [(4-bromophenyl)methylene]bis (4-hydroxy-2h-1-benzopyrane-2-one)

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Complexes of coumarin derivate 3, 3'-[(4-bromophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyrane-2-one), with some lanthanoid ions Ln(III) = La(III), Nd(III), Eu(III), Gd(III), and Tb(III) were synthesized. The complexes obtained were characterized by means of elemental analysis, IR spectroscopy, UV-Vis spectroscopy, fluorescence spectroscopy and microscopy. The spectral data of the synthesized complexes were interpreted on the basis of comparison with the spectra of the free ligand in order to determine the mode of coordination in the complexes. Results from the IR spectra suggested that the coordination is through the carbonyl oxygen atom as well as through the deprotonated hydroxyl group. The complexes possess optical properties shown by their absorption in the UV/Vis region. The excitation and emission spectra of Tb(III) complex were taken in solid state. The lifetime of the excited state was measured.

Key words: Lanthanoids, Complexes, Biscoumarins, IR spectroscopy, Optical properties.

INTRODUCTION

The coumarin (also known as 1,2-benzopyrone) and its derivatives are a large class of chemical compounds with arising interest during the last few years. Most of them are naturally occurring and can be found in plants, bacteria and fungi [1, 2]. Coumarin compounds can be synthesized using different chemical methods such as Pechman reaction [3, 4], Knoevenagel condensation [5, 6], and etc. Different types of substitution of the parent ring suppose that coumarins are extremely variable in structure resulting in large variety in their properties. Some of them are used as drugs in medicine [7, 8], as well as pharmacological agents [9-11]. Coumarins can be used as optic agents, since fluorescent coumarin derivatives have been widely used in many applications from cell biology, medicinal analysis, lasers, and sensors to the advanced photochemical systems [12-15], because of their extended spectral range, high emission quantum yields, photostability, and good solubility in the safest solvents.

Recently coumarin compounds have been investigated for their coordination ability. In literature there is a lot of data concerning coordination properties of coumarins towards different metal ions [16-19]. It is important to understand the relationship between structure of the synthesized metal complexes and their properties.

Some authors have observed the influence of the complexation on biological properties; they pointed out that the metal ion can improve the biological activity of the investigated compounds [20-22]. Other articles have described the influence of the metal ion on their spectroscopic properties [22-24].

During last few years compounds of 3,3'-benzylidene-bis[4-hydroxycoumarin] with different substitution in the benzylidene ring have been synthesized and investigated [25-27]. Synthesis of their lanthanoid complexes is another area of scientific interest. The synthesized complexes were investigated by different physicochemical methods and molecular modeling methods [27, 28]. Their pharmacological properties were also tested [29]. Complexes showed good optical properties, which can be well-preserved after their immobilization in different matrices [23, 30].

In the current research we used the coumarin compound 3,3'-[(4-bromophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyrane-2-one), C₂₅H₁₅O₆Br. It belongs to the group of 3,3'-benzylidene-bis(4-hydroxy-2H-1-benzopyrane-2-one) derivatives, with different substitutes like –OH, –NO₂, –OCH₃, –Cl, etc. This compound (named for short L15-Br) possess –Br substitute on *para* position in the benzylidene ring (Fig. 1).

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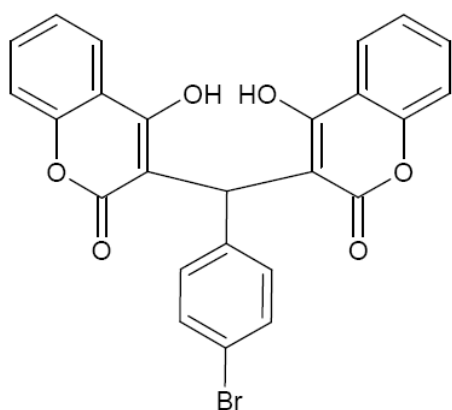


Fig. 1. Chemical formula of 3,3'-[(4-bromophenyl)-methylene]bis-(4-hydroxy-2H-1-benzopyrane-2-one), (L15-Br)

We synthesized complexes of L15-Br with some lanthanoid ions – La(III), Nd(III), Eu(III), Gd(III), and Tb(III) – and studied their structures and properties by physicochemical methods.

EXPERIMENTAL

Chemicals used for the experiments were of analytical grade. A coumarin compound 3, 3'-[(4-bromophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyrane-2-one), $C_{25}H_{15}O_6Br$, synthesized by Knoevenagel condensation [31], was used as a ligand.

Metal salts used were lanthanoid nitrates hydrates, among them $Nd(NO_3)_3 \cdot 6H_2O$ was purchased from Fluka, $La(NO_3)_3 \cdot 6H_2O$ was purchased from Merck, both were of p.a. grade. The others like $Tb(NO_3)_3 \cdot 7H_2O$, $Eu(NO_3)_3 \cdot 8H_2O$, $Gd(NO_3)_3 \cdot 9H_2O$ were prepared by dissolving the lanthanoid oxides in diluted nitric acid, followed by crystallization and recrystallization. The hydrated water was determined by complexometric titration. Ethyl alcohol, dimethyl sulfoxide and acetone were used as solvents.

Complexes were synthesized in two steps. As a first step the ligand was dissolved in water/ethanol solution under magnetic stirring and 1M NaOH (aqueous solution) was added dropwise in order to deprotonate a hydroxyl group of the ligand. The stirring continued until complete dissolution of the ligand. To the solution formed, as a second step, the ethanol solution of the lanthanoid nitrate was added dropwise. The suspension obtained was kept stirred for 3 hours, and then filtered and washed several times with water. The drying in a desiccator to constant mass resulted in a powder probe. All the samples were recrystallized by acetone, except Eu(III) complex, which was recrystallized by ethanol.

The complexes synthesized were characterized by automatic analyzer EuroEA 3000, which allows

simultaneous determination of the content of carbon, hydrogen and nitrogen in samples of organic compounds and materials. The content of the metal ion was determined by complexometric titration in ethanol media.

The IR spectra of the ligand and the complexes were registered in KBr pellets with a diameter of 13 mm. The spectra were recorded on a Thermo Scientific Nicolet iS5 Fourier-Transform IR spectrometer (DTGS detector) at a spectral resolution of 2 cm^{-1} and accumulation of 64 scans. The spectra were scanned in the $4000 - 400\text{ cm}^{-1}$ range.

Optical properties were investigated with an Evolution 300 UV-Vis spectrometer (Thermo Scientific) and a Cary Eclipse spectrometer with a xenon lamp as the excitation source as well as on an N-400M fluorescence microscopy.

RESULTS AND DISCUSSION

Elemental analysis

The elemental analysis data obtained served as a basis for determination of empirical formulae of the compounds. It turned out that there is a good agreement between the calculated values and the found. On that base we suggested that every lanthanoid ion binds with three molecules of the ligand and different number of water molecules, in agreement with preferred high coordination number of the metal ion. The so synthesized complexes are proposed to be with $Ln(HL)_3 \cdot nH_2O$ stoichiometry for La(III), Nd(III), Eu(III), Gd(III), Tb(III), where $HL = (C_{25}H_{14}O_6Br)^-$ is the mono-deprotonated form of the ligand, since sodium hydroxide was used in synthetic procedure. The complexes were found to be soluble in dimethyl sulfoxide, dichloromethane, and dimethylformamide, slightly soluble in ethanol but insoluble in water. The elemental composition (in %), the formulae with the coordination water included as well as the respective symbols used for the complexes, are presented below:

LaL15-Br, $La(HL)_3 \cdot H_2O$; %C (55.34/55.52), %H (2.72/3.32), %La (8.53/7.98),

NdL15-Br, $Nd(HL)_3 \cdot 3H_2O$; %C (53.96/53.08), %H (2.89/3.34), %Nd (8.64/8.73),

EuL15-Br, $Eu(HL)_3 \cdot H_2O$; %C (55.41/54.88), %H (2.89/2.68), %Eu (9.10/9.27);

GdL15-Br, $Gd(HL)_3 \cdot 2H_2O$; %C (54.13/54.15), %H (2.78/3.05), %Gd (9.44/9.99),

TbL15-Br, $Tb(HL)_3 \cdot 2H_2O$; %C (54.07/53.87), %H (2.78/3.03), %Tb (9.54/9.24).

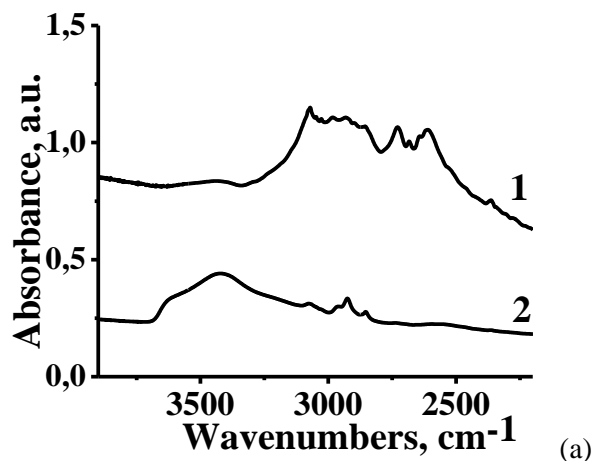
Infrared spectroscopy of the free ligand and NdL15-Br

Our efforts for single crystals preparation of the complexes turned out to be unsuccessful. That is

why a vibrational analysis was used as an opportunity to reveal the possible mode of coordination. The infrared spectra of the complexes were interpreted on the basis of the comparison with the spectrum of the free ligand.

The IR spectra of the ligand L15-Br (1) and NdL15-Br (2) in the range 3900-1800 cm^{-1} (a) and in the range 1700-1200 cm^{-1} (b) were recorded (Figure 2). In the spectrum of the free ligand intensive bands at 1669 cm^{-1} and 1617 cm^{-1} were observed, which can be assigned for the carbonyl oxygen atom (C=O) [27, 32]. The bands observed are lower than the shift for the free carbonyl group [27, 32]. That fact can be attributed to the participation of the carbonyl group in stable C=O \cdots H bridges. In the spectra of the complexes these bands were shifted to lower wavenumbers. The band observed at 1598 cm^{-1} in the spectrum of NdL15-Br can be attributed to the ν_{sym} (C=O) [33]. That band is the most informative about the participation of the oxygen atom from the carbonyl group in coordination with Ln(III) ion. The shoulder observed at 1620 cm^{-1} can be assigned to the asymmetric vibration of the carbonyl group [27, 32]. Bands appearing at 1605, 1562, 1486 and 1455 cm^{-1} in the spectrum of the ligand corresponded to the vibration of the phenolic ring. In the spectrum of the complex they were shifted to lower wavenumbers.

In the IR spectrum of the ligand the weak band at 3073 cm^{-1} can be assigned to the $\nu(\text{OH})$ vibrations [27, 32]. This band was not observed in the spectrum of the complex, indicating that the deprotonated form was involved in complexation. The broad band in the range 3750 – 3100 cm^{-1} , observed in the spectrum of NdL15-Br (Figure 2, a 2), was assigned to the $\nu(\text{O-H})$ vibrations of coordinated water [27, 32] and did not appear in the spectrum of the ligand.



The spectral behavior of the complexes synthesized is similar. So based on that reason we can conclude that the coordination of the lanthanoid ion is identical in the formed complexes, i.e. they are isostructural. The coordinated water registered by IR spectra supports the elemental analysis data and the proposed empirical formulae of the complexes. The coordinated water molecules along with the three molecules of the mono-deprotonated ligand in Ln(HL)₃ reassure a coordination number higher than six for the lanthanoid ion. This is in a good agreement with the high coordination numbers known for the lanthanide ions [34].

Electronic spectra

The absorption spectra of the free ligand and its Ln(III) complexes were recorded (Figure 3). Compared to the UV-Vis spectrum of the ligand, changes are observed in the spectra of the complexes. In the spectrum of the free ligand an intense broad band from 260 to 337 nm, indicating a π - π^* transition is observed. The complexes absorb throughout the interval 200-900 nm with local maxima in the UV region up to 350 nm and in the visible region (for NdL15-Br).

In the absorption spectrum of NdL15-Br (Figure 3) a broad band around 300 nm with intensity lower than the one observed in the ligand. That band can be assigned to the transition in the ligand. Bands with lower intensity due to f-f transitions appeared at region 430-900 nm. The absorption bands of Nd(III) in the visible and NIR region appear due to transitions from the ground levels of $^4I_{9/2}$ to the excited J- levels of the 4f configurations [35].

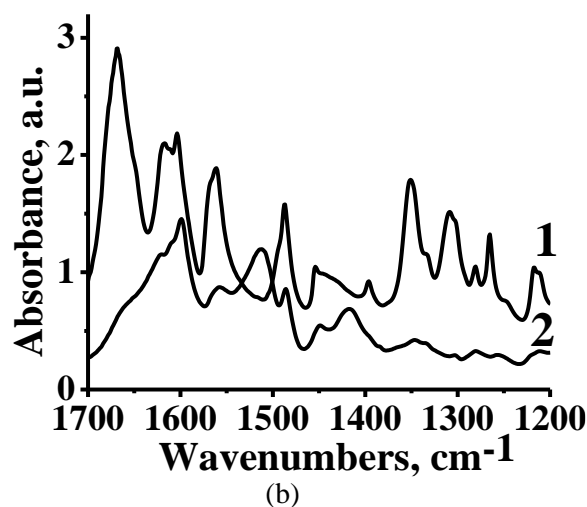


Fig. 2. IR spectra of the ligand (1) and NdL15-Br (2) in the range 3900-1800 cm^{-1} (a) and in the range 1700-1200 cm^{-1} (b)

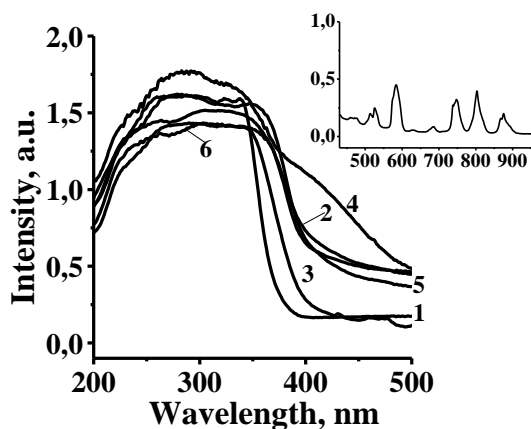


Fig. 3. UV - Vis spectra of the free ligand (1) and the complexes LaL15-Br (2), NdL15-Br (3), EuL15-Br (4), GdL15-Br (5), TbL15-Br (6), inset f-f transitions for NdL15-Br

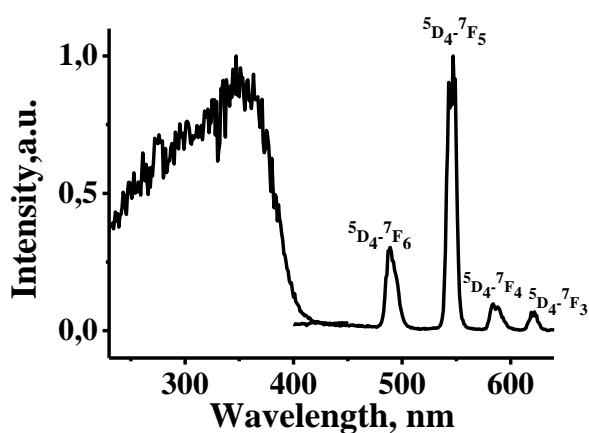


Fig. 4. Excitation and emission spectra of powdered terbium complex

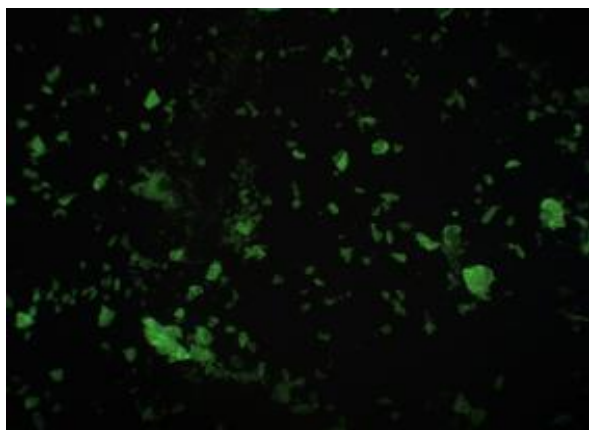


Fig. 5. Fluorescent microscope image for the sample of TbL15-Br

Excitation and emission spectra

The luminescence nature of Ln(III) ions is well known, but still an interesting area in the science investigations [36]. Complexes of Ln(III) with optical properties usually consist of organic molecules, capable of transferring energy to the metal ion and overcoming their low extinction coefficient [34]. In case of ion with luminescence in

visible region, such as Tb(III) ion, the organic component should be excited in the UV area, allowing effective charge transfer from the ligand to the metal ion.

The luminescence properties of the powdered probe of TbL15-Br complex were investigated under ultraviolet excitation.

The excitation spectrum was recorded with excitation maximum around 350 nm (Figure 4). The emission spectrum (Figure 4) showed characteristic emission bands of the Tb(III) ion at about 489 nm ($^5D_4-^7F_6$), 583, 588 nm ($^5D_4-^7F_4$) and 621 nm, corresponding to $^5D_4-^7F_3$ transitions. The transition $^5D_4-^7F_5$ is presented with an intensive emission band splitted at 543, 547 and 548 nm. Transitions are from the lowest excited state 5D_4 of Tb(III) ion to the highest ground state 7F_0 and next 7F_1 ($J=0-6$) [23]. Green emission of Tb(III) was observed with fluorescence microscopy, and it is concerned as reliable proof for presence of the ion (Figure 5). The lifetime of the excited state of powdered probe of TbL15-Br was found to be 465 μ s.

Obviously the content of water in the inner sphere of Tb(III) complex did not interfere its fluorescence. That was not the case with the other complexes. For example complex of Eu(III) did not show any luminescence under UV light irradiation, probably because of the water content. It is well known that the photophysical properties of Eu(III) ion and Tb(III) ion markedly depend on their environment, i.e. the luminescence is strongly decreased by the presence of water molecules in the coordination sphere [37]. Besides, excitation and absorption spectra matched for Tb(III) complex only, suggesting that the charge transfer from the ligand to Eu(III) was not enough to sensitized the metal ion.

CONCLUSION

Complexes of coumarin derivate 3,3'-[(4-bromophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyrane-2-one) with some lanthanoid ions such as La(III), Nd(III), Eu(III), Gd(III), and Tb(III) were successfully synthesized. The IR-spectra elucidated the possibilities for coordination of the metal ion to the OH deprotonated and the C=O oxygen atom. The Tb(III) complex of 3,3'-[(4-bromophenyl)methylene]bis-(4-hydroxy-2H-1-benzopyran-2-one) showed luminescent properties.

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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА ЛАНТАНОИДНИ КОМПЛЕКСИ С 3,3'- (4-БРОМОФЕНИЛМЕТИЛЕН)БИС(4-ХИДРОКСИ-2*H*-1-БЕНЗОПИРАН-2-ОН)

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(Резюме)

Синтезирани са комплекси на 3,3'-(4-бромобензилметилена)бис(4-хидрокси-2*H*-1-бензопиран-2-он) с някои лантаноидни йони Ln(III) = [La(III), Nd(III), Eu(III), Gd(III), Tb(III)]. Получените комплекси са охарактеризирани с помощта на елементарен анализ, ИЧ спектроскопия, UV-Vis спектроскопия, флуоресцентна спектроскопия и микроскопия. Спектрите на комплексите са сравнени с тези на свободния лиганд, за да може да бъде направено предположение за начина на координиране на металния йон към лиганда. Данните от ИЧ-спектъра на комплексите ни дават основание да предположим, че металният йон координира с карбонилния кислороден атом, както и с депротонираната хидроксилна група на лиганда. Оптичните свойства на комплексите са показани чрез абсорбция в UV- Vis областта. Регистрирани са спектрите на възбуждане и емисия на прахова проба на Tb(III) комплекс. Измерено е времето на живот във възбудено състояние за праховата проба.

Ключови думи: Лантаноиди, Комплекси, Бискумарини, ИЧ спектроскопия, Оптични свойства