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Complexes of La(III), Sm(III), Tb(III), Dy(III), Ho(III) and Er(III) Ions with Morin

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New solid complex compounds of La(III), Sm(III), Tb(III), Dy(III), Ho(III) and Er(III) ions with morin were obtained. They were characterized by elemental analysis, thermogravimetric studies and spectrophotometric determination of metal ions. The molecular formulae of the compounds are: $Ln(C_{15}H_9O_7)_3 \cdot nH_2O$, where n = 6 for La, Sm, Tb, Dy and n = 5 for Ho and Er. Low molar conductances of the complexes (which correspond to non-electrolytes) and the π-π* bands of ligand and the CT bands L→M in UV-VIS spectra of the methanol solutions of the complexes were established. On the basis of ^{13}C NMR and IR spectra, it was supposed that morin was bound to the lanthanide ions *via* C(4)=O and C(3)–oxygen.

Key words: morin, lanthanides, complexes, thermogravimetric analysis, spectroscopic properties, conductivity

Morin (3,5,7,2′,4′-pentahydroxyflavone), Fig. 1, belongs to a group of natural plant dyes, called flavonoids. Due to a convenient position of oxygen in the C(5)–OH and C(4)=O as well as C(3)–OH and C(4)=O groups, morin forms chelate complexes with ions of p-, d-, and f-electron metals. Complexation reactions are sensitive and the mole absorption coefficients are of the order of 10^4, therefore, morin was applied in analytical practice to spectrophotometric and fluorimetric metal ions determinations [1].

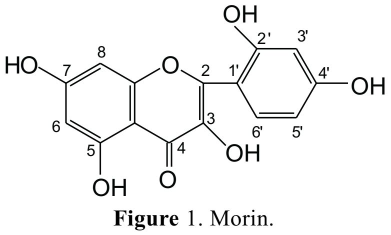

Figure 1. Morin.

Morin has also been used for thorium identification in the presence of rare earths elements, and also for a simultaneous determination of cerium and yttrium [3]. In [4], morin–diantypirylomethane complexes (DAM) of lutetium and other lanthanides were tested and it was found that among them only lanthanum, gadolinium and lutetium form complexes with luminescence properties. That is because of lack of electrons 4f (La) shell in their ions or completely filled with electrons 4f (Lu) shell, as well as a highly excited state in gadolinium ion. Extraction of the whole lanthanide group with morin was investigated [5]. The extraction constants were determined and their dependence on the lanthanide number was given. Furthermore, a complex of La(III) with morin was used for fluorescence determination of DNA [6]. However, the solid lanthanide(III) ions complexes of morin were discussed only in [7]. The authors presented the synthesis and a spectral study of the complexes of morin with: La, Ce, Pr, Nd, Eu. They determined the composition of the complexes, namely $Ln(C_{15}H_{10}O_7)_2Cl_3$. They also established, that oxygen of C(5)–OH and C(4)=O groups participates in binding the lanthanide ions.

In this paper, we report the synthesis and spectral characterization of new La(III), Sm(III), Tb(III), Dy(III), Ho(III) and Er(III) complexes with morin in solid state. The composition of the complexes and their structure are proposed. The obtained compounds exhibit strong luminescence properties and some of them may be potentially used in laser technology.

EXPERIMENTAL

Reagents: $1\cdot10^{-2}$ mol/dm^3 morin solution ($C_{15}H_{10}O_7\cdot2H_2O$ International Enzymes LTD) was prepared by dissolving an appropriate weighed amount of morin in methanol. Solutions of metal chlorides ($1\cdot10^{-2}$ mol/dm^3) were obtained by dissolving an appropriate weighed amounts of the oxides (99.9%): La_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3 in concentrated hydrochloric acid. The excess of the acid being evaporated and the rest dissolved in redistilled water. $1\cdot10^{-2}$ mol/dm^3 samarium nitrate(III) (99.9%) was obtained by dissolving an appropriate weighed amount of the compound in redistilled water. All the other reagents: xylenole orange – indicator, chloric acid (VII), NaOH and dimethylsulfoxide (DMSO) were analytically pure.

Synthesis of the complexes: 50 cm^3 of the stock solutions of the salt of lanthanide ions ($c = 1\cdot10^{-2}$ mol/dm^3) was added into 150 cm^3 of hot saturated solution of morin in methanol ($c = 1\cdot10^{-2}$ mol/dm^3) and diluted with water in 1:1 ratio. The obtained solution was stirred and pH within 4–5 was fixed with 0.1 mol/dm^3 NaOH solution. Then the mixture was heated to 60°C for 1h and left at room temperature for 24 h. The precipitated sediments were separated and washed several times with water and water–methanol (1:1) solution. Then the sediments were dried in air at room temperature and yellow amorphous compounds were obtained.

Analysis: The amounts of C and H in the investigated compounds were determined with a Carbo-Erba EA-1108 apparatus for elemental microanalysis. The metal content was determined spectrophotometrically with xylenole orange [8]. The water content in the complex was determined by gravimetric methods and derivatography. Analyses confirmed the compositions proposed.

Thermogravimetric analysis: Thermogravimetric study was performed in air with an OD-102 derivatograph, F. Paulik – J. Paulik – L. Erdey system (MOM, Hungary) under the following conditions: TG-100 mg, DTA-1/5, DTG-1/10, with 10 deg/min speed. The thermogravimetric results of experiments for all studied compounds are collected in Table 1.

Spectral measurements: UV and VIS spectra of the complexes in methanol were carried out using a Beckman DU 640 spectrophotometer, Fig. 2. IR spectra within the range of 4000–500 cm^{-1} were made in KBr pellets on an FT–IR Paragon-1000 spectrophotometer (Perkin–Elmer, USA). The results of infrared spectral examination of morin and all compounds are listed in Table 2. Table 3 shows the values of the chemical shifts, δ, of the bands in ^{13}C NMR spectrum of the La(III)–morin complex. The ^{13}C NMR spectra of morin and La(III)–morin complex have been recorded with a Bruker AM 500 instrument in dimethylsulfoxide-d_6 at room temperature.

Table 1. Results of thermal decomposition of the lanthanide complexes with morin.

Compound	ΔT_1 [°C]	T_{min}^{DTG}	ΔT_2 [°C]	T_k [°C]	nH_2O	% H_2O		% residue mass		Final decomposition product
						Calc.	Obtained	Calc.	Obtained	
$La(C_{15}H_9O_7)_3 \cdot 6H_2O$	20–170	100	170–780	780	6	9.4	9.5	14.2	14.5	La_2O_3
$Sm(C_{15}H_9O_7)_3 \cdot 6H_2O$	20–170	90	170–900	900	6	9.3	9.5		20.5	
$Tb(C_{15}H_9O_7)_3 \cdot 6H_2O$	20–170	90	170–900	900	6	9.2	8.5	15.9	16.0	Tb_4O_7
$Dy(C_{15}H_9O_7)_3 \cdot 6H_2O$	20–160	80	160–870	870	6	9.2	10.0	15.8	15.0	Dy_2O_3
$Ho(C_{15}H_9O_7)_3 \cdot 5H_2O$	20–160	80	160–760	760	5	7.8	8.0	16.3	15.0	Ho_2O_3
$Er(C_{15}H_9O_7)_3 \cdot 5H_2O$	20–160	80	160–730	730	5	7.8	8.0	16.5	15.0	Er_2O_3

ΔT_1 (ΔT_2) – temperature range corresponding to dehydration endoeffect of definite amount of water molecules (corresponding to composition of anhydrous compound).
T_{min}^{DTG} – temperature corresponding to minimum on DGT curve.
T_k – temperature of final product formation.

Table 2. Position of the most important bands in IR spectra at morin and its complexes with lanthanides(III).

Kinds of bonds	morin cm^{-1}	La complex cm^{-1}	Sm complex cm^{-1}	Tb complex cm^{-1}	Dy complex cm^{-1}	Ho complex cm^{-1}	Er complex cm^{-1}
Stretching vibrations OH in H_2O molecules and –OH group forming hydrogen bonds	3370 3147	3230	3375 3330	3390 3265	3376 3241	3318 3264	3363 3229
Valence band C=O	1664	1652	1650	1652	1652	1652	1652
Stretching vibrations C=C in aromatic ring, ring vibrations	1630 and 1611 – 1508 1455–1459	1601 1548* 1508 1441	1600 1546* 1503 1436	1600 1548* 1507 1441	1600 1548* 1507 1444	1600 1548* 1507 1444	1599 1548* 1507 1442
Deformation vibrations -C-OH	1379 1355 1310	1368 – 1321 –	1365 – 1321 –	1366 – 1325 –	1366 – 1325 –	1366 – 1325 –	1365 – 1323 –
Stretching vibrations -C-OH	1257 1226 1202 1175 1085 – 1011	– 1238 1198 1172 – 1095 1007	– 1236 1198 1171 – 1095 1007	– 1238 1198 1174 – 1096 1007	– 1238 1199 1174 – 1095 1007	– 1239 1199 1173 – 1096 1008	– 1238 1199 1171 – 1095 1007
Deformation vibrations – C-H outside plane, related to substitution of aromatic rings of multiring compounds	970 875 – 795 634 585 566	975 884 805* 795 646 584 567	973 884 804* 795 648 594 568	975 885 810* 795 650 588 568	976 885 810* 795 650 589 568	976 886 810* 795 650 588 568	974 886 809* 795 649 588 568
Stretching vibrations M–O	–	492*	495*	501*	501*	504*	501*

* – new band.

Conductivity measurements: Molar conductances of $1 \cdot 10^{-3}$ mol/dm^3 DMSO solutions of lanthanide(III) complexes at room temperature were measured with a Hach conductivity TDS Mater.

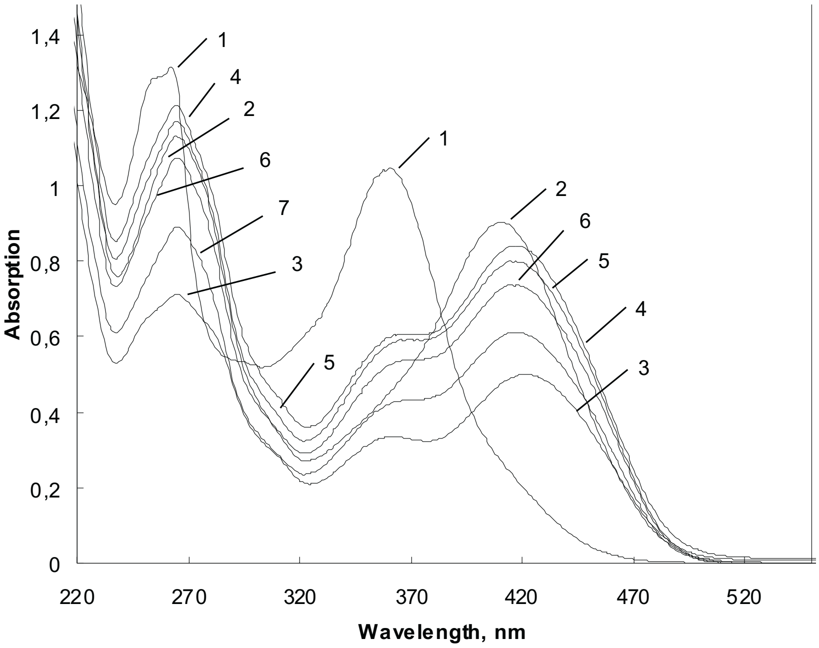

Figure 2. Electronic absorption spectra of morin and its complexes with lanthanide ions in methanol: 1 – morin, 2 – La(III), 3 – Sm(III), 4 – Tb(III), 5 – Dy(III), 6 – Ho(III), 7 – Er(III). Concentrations of solutions: curve 1 – $5.9 \cdot 10^{-5}$ mole/dm^3, curves 2, 4, 5, 6, 7 – $1.7 \cdot 10^{-5}$ mole/dm^3, curve 3 – saturated solution, l = 1 cm, reference – CH_3OH.

Table 3. Values of the chemical shifts δ in carbon range for morin and La–morin complex.

C	Morin [13] δ, ppm	Morin δ, ppm	La–morin complex δ, ppm	$\Delta\delta$ morin–La complex
2	149.63	148.97	148.08	+0.89
3	136.49	136.45	143.40	–6.95
4	176.71	176.35	179.01	–2.66
5	156.94	156.88	156.53	+0.35
6	94.99	93.40	93.23	+0.17
7	164.10	163.68	163.28	+0.40
8	99.57	98.06	97.84	+0.22
9	161.31	161.01	160.63	+0.38
10	104.97	106.90	107.13	–0.23
1′	111.19	115.48	112.38	+3.10
2′	158.09	157.08	158.87	–2.79
3′	104.97	103.62	102.77	+0.85
4′	160.97	160.52	159.87	+0.65
5′	109.25	109.53	107.12	+2.41
6′	132.31	131.49	128.50	+2.99

RESULTS AND DISCUSSION

Synthesis of the complexes of La(III), Sm(III), Tb(III), Dy(III), Ho(III) and Er(III) with morin: The synthesis was done using aqueous – methanol solutions (1:1) at c_M:c_L = 1:3 (c_M – molar concentration of metal ion, c_L – molar concentration of ligand). The complexes were isolated as water solvates with the molecular formulae $Ln(C_{15}H_9O_7)_3 \cdot nH_2O$, where Ln is cation of lanthanide, n = 6 for La, Sm, Tb, Dy and n = 5 for Ho and Er. The compounds are yellow and amorphous. They are insoluble in water and sparingly soluble in other polar solvents (methanol, ethanol and acetonitrile). For this reaction the molar conductances of their $1 \cdot 10^{-3}$ mol/dm^3 DMSO solutions were determined to change from 6.0 Ω^{-1} cm^2 mol^{-1} for La to 4.0 Ω^{-1}cm^2 mol^{-1} for Ho and Er. Such low conductances correspond to non-electrolytes [9]. Similar results were obtained in [10] for complexes of morin with Co(II), Ni(II), and Cd(II).

Thermogravimetric analysis: Thermogravimetric measurements confirmed the elemental analysis results and the composition of the obtained complexes. The temperatures of the decomposition of the investigated compounds (Table 1) indicate, that the compounds undergo a gradual decomposition with the temperature increase.

All hydrated complexes decompose in two steps. They dehydrate within the temperature range 20–170°C, losing all crystallization water. This suggests that the obtained complexes contain only outer sphere water. The dehydration process is endothermic, further increase of temperature causes exothermic processes of combustion of ligand in aerobic conditions, eventually leading to lanthanide oxides: Ln_2O_3, where Ln = La, Dy, Ho and Er and Tb_4O_7. The final decomposition product (890°C) of samarium(III) complex is difficult to unequivocal determination. Taking into account the qualitative chemical analysis of the residue and its white colour it seems that the final product is a mixture of oxocarbonates.

Electronic spectra: There are two intensive absorption bands in the UV-VIS spectrum of morin in methanol; the band centered at 359 nm is due to transition localized within B ring of cinamonyl system, whereas that one centered at 262 nm is consistent with absorbance of ring A of benzoyl system [11]. They are related to the π-π^* transitions. All the electronic absorption spectra of the methanol solutions of the complexes are similar, Fig. 2. The characteristic feature of the electronic spectra of the lanthanide(III) complexes of morin is batochromic shift of all the bands (band λ_{max} = 352 nm by 4–9 nm and band λ_{max} = 262 nm by 3–5 nm) and the presence of a new intensive band in the visible range of λ = 415–417 nm. The band is related to the L→M charge-transfer. Molar absorption coefficients of charge-transfer bands in the complexes are of the order of $4 \cdot 10^4$.

IR spectra: IR spectra of the complexes at 4000–500 cm^{-1} exhibit a large similarity, suggesting a similar structure. Table 2 shows the position of the most important IR bands of morin and its complexes with lanthanides(III). Comparing the IR spectra of morin and its complexes, one can notice their large frequency differences. Almost each band in the complex is shifted towards lower frequencies (with relation to morin) and only some of the bands undergo a shift towards higher frequencies. There also appear new bands in the complexes, due to the formation of the M–O bond. These are the bands of the frequencies: 1546–1548 cm^{-1}, 804–810 cm^{-1} and 492–504 cm^{-1}. The 1546–1548 cm^{-1} band is related to the formation of the chelate ring >C=O· · ·M–O– [12]. The most characteristic stretching vibration in infrared spectra of morin and their complexes is the $\nu_{(C=O)}$, which is centered at 1664 cm^{-1} in the case of morin and shifted to 1650–1652 cm^{-1} for the complexes. Thus, it may be assumed that the C=O group participates in binding the lanthanide ion.

^{13}C NMR spectrometry: The ^{13}C NMR of morin and the lanthanum–morin complex have been recorded in DMSO-d_6 solvent at room temperature. The assignment of morin carbons, indicated on the spectrum, has been made by considering available literature data [13]. The feature of the complex spectrum is that the complex formation of morin affects the resonance of each carbon atom. The most important differences are observed for C(3) and C(4), which are shifted downfield by 6.95 and 2.66 ppm, respectively. This is connected with a decrease of the electronic deficiency on C(3) and C(4). This reduction could be explained by a decrease of C(4)=O and C(2)=C(3) bonds orders after complexation [14]. The relative positions of the three morin molecules of the complex could also lead to changes in the chemical environment of the lateral phenyl ring. The change of the rotation and rocking of this ring creates different intra-molecular interactions. This explains the difference between phenyl ring resonances of La(III)–morin complex and morin.

Structure of the complexes: Morin has two possibilities of binding the metal ion: the first in based on C(3)–OH and C(4)=O system and the second – *via* C(5)–OH and C(4)=O. If the metal ion is bound to morin *via* C(4)=O and C(3)–O, the most stable five-element chelate compounds are formed. In the other case, the less stable six-element chelates arise. The ^{13}C NMR spectrum of the La(III)–morin complex helps to determine, which oxygen of morin groups C(3)–OH or C(5)–OH takes part in binding the lanthanide ions. The comparison of the chemical shifts of the complex with that of morin gives the largest difference values for C(3), $\Delta\delta = 6.95$ ppm, which points that in this complex the metal is bound in C(3)-oxygen position. The coordination mode of morin could be interpreted on the basis of infrared spectral comparison between the lanthanide-morin, lanthanide-quercetin-5′-sulfonic acid and lanthanide–chrysin complexes. The position of the $\nu_{(C=O)}$ group in the studied complexes occurs at 1650–1652 cm^{-1}. Similar frequency values of the C(4)=O group are shown by the complexes of quercetin-5′-sulfonic acid with lanthanides [15], where oxygen of the C(3)–OH and C(4)=O groups participate in binding metal. However, in chrysin–lanthanide complexes, the carbonyl group band occurs at 1635 cm^{-1} and oxygens of the groups C(5)–OH and C(4)=O take part in binding metal [16]. Comparable value of $\nu_{(C=O)}$, 1638 cm^{-1}, is obtained in [7], where Ln(III) ions are bound to morin in the same way as in the case of chrysin (*via* C(4)=O and C(5)–O). On the basis of spectral data, we conclude that in the complexes under investigation morin is chelated to the central metal ion *via* C(4)=O and C(3)–O oxygen donors. Moreover, IR spectra of the tested hydrated and dehydrated complexes are identical, so it should be assumed that water present in the compounds is the crystalline water and is not present in the inner coordination sphere of the complex. Hence, the coordination number of the Ln(III) ion should be 6. Based on the above studies, we propose a tentative coordination structure for the complexes, shown in Fig. 3.

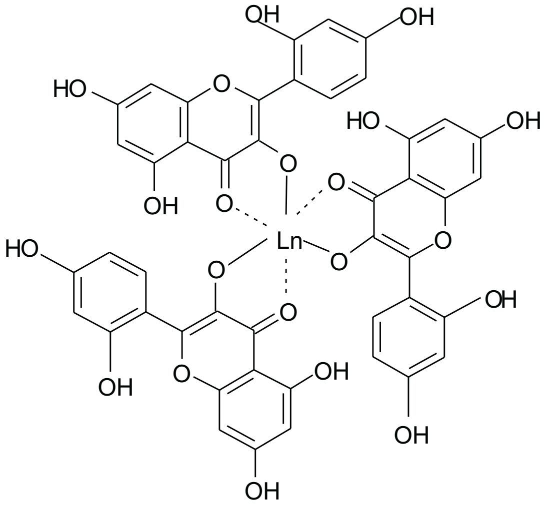

Figure 3. Proposed structural formula of lanthanide complexes with morin, Ln – lanthanide ion.

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