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New solid compounds of Tb(III), Ho(III), Er(III) and Yb(III) with chrysin

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Abstract New solid compounds of Tb(III), Ho(III), Er(III) and Yb(III) with chrysin were synthesized and characterized by elementary analysis, thermogravimetric studies and magnetic measurements. The molecular formula of the complexes is $Ln(C_{15}H_9O_4)_3 \cdot 4H_2O$ where Ln is the cation of lanthanides. The oxidation state of metal ion in the complexes does not change and equals +3. The thermogravimetric analysis shows that two water molecules are present in the inner coordination sphere of the complex and the two molecules are in the outer sphere. The structure of the complexes was determined on the basis of UV–visible, IR and ^{1}H NMR spectroscopies. It was found that chelation of the metal ion occurs at the 5-hydroxy-4-keto site.

Keywords Chrysin · Lanthanide complexes · Spectroscopic properties · Thermal analysis

Introduction

Flavonoids are phenolic compounds widely distributed in plants. Over 4000 of these compounds have been isolated and identified from both higher and lower plants and the list constantly expands. The best know are quercetin, morin and rutin. Some flavonoids compounds are contained in pharmaceuticals and applied in the therapy [1–3]. A great number of flavonoids are able to chelate metal ions; and often the presence of 3-hydroxyl group or 5-hydroxyl group allows the complex formation involving the carbonyl function. These complexes often play a crucial role in some biological functions [4, 5] and their activities are often higher than those of the parent compounds [6]. Flavonoids are also used in chemistry as colorimetric reagents for the detection of metals traces in solutions [7].

Chrysin, one of the lesser-know flavonoids, possesses a broad range of pharmacological properties including anti-oxidant, anti-allergic, anti-inflammatory and anti-cancer activities [8, 9]. It has been also demonstrated that chrysin and its complex with La(III) can both bind to DNA [10] and have inhibiting effects against two kinds of tumor cells (A-594 and P388). At 10 µM concentration the inhibitory ratios of La(III) complex against the tested tumor cells were higher than those of chrysin. Furthermore, the complexes of La(III), Gd(III) and Eu(III) ions with quercetin show antitumor activity (blood cancer, human colon, liver, prostate, lung cancer) [6]. It seems that, these complexes react with DNA changing the transcription of DNA and repressing the growth of tumour cells, which is the basis of designing new and more efficient antitumor drugs. So, the study of the synthesis of rare earth metals chrysin complexes appeals very much to our interest.

In our previous works [11–13], the complexes of chrysin with Al(III), Ga(III), In(III), Ti(IV), Zr(IV), Co(II), Ni(II), Cu(II) and Zn(II) were examined as solids.

This paper describes the synthesis of the solid compounds of Tb(III), Ho(III), Er(III) and Yb(III) with chrysin. Elementary and thermogravimetric analyses were

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performed to determine the composition of the compounds. The structure of the complexes was deduced based on the results of visible and infrared as well as the ^{1}H NMR spectroscopies.

Experimental

Materials

The stock solutions of lanthanide chlorides were prepared by dissolving an appropriate weighed amount of the following salts: $TbCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$, $ErCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ in of bi-distilled water.

A saturated solution of chrysin in methanol was obtained by heating of weighed amount of chrysin in 100 ml of methanol. After cooling the remaining undissolved residue was filtered off and solubility of chrysin was quantified based on spectrophotometric determination. All the other reagents were analytically pure.

Synthesis of the compounds

The complexes of chrysin with Tb(III), Ho(III), Er(III) and Yb(III) were obtained by the procedure described below. In particular, 150 cm^3 of hot saturated solution of chrysin and 40 cm^3 methanol was added into 40 cm^3 of the water solution of the appropriate lanthanide chlorides with continuous stirring, to reach M:L = 3:1 molar ratio. The solutions was stirred and the pH was fixed 5.5–6.0 with sodium hydroxide solution. The precipitate was formed, which was washed with copious amount of hot water–methanol (1:1) solution to remove Cl$^-$ ions, separated by centrifuging and dried in air at room temperature. The complexes thus prepared and their yields (η) are given in Table 1.

Instrumentation and measurement

Elemental analysis for C, H was performed with an Elemental Analyzer EA 1108 apparatus (Carb Erba). The content of metals in the studied compounds was obtained by two independent methods. Metal ions were determined by classic spectrophotometric method in the presence of xylene orange as indicator [14], then the samples were dissolved in perchloric acid. In separate experiments the metals were quantified by TG analysis. The final mass of the metal oxides obtained by heating the samples at 1,253 K was recalculated for metal ion percentage. The results obtained are listed in Table 1. The solubilities of the Tb(III), Ho(III), Er(III) and Yb(III) compounds in methanol at 298 K were determined by measuring the concentration of compounds in saturated solution using UV–vis spectroscopy. Molar conductances at 298 K were measured in 10^{-3} M DMSO and DMF solution using a CPC-551 type conductivity meter. The thermogravimetric study was performed with a Setsys TG-DSC 15 apparatus between 20–1,000 °C in nitrogen atmosphere and in air with a F. Paulik–J. Paulik–L. Erdey 3427 T derivatograph (MOM, Hungary) at a heating rate 10° min^{-1}. The UV–vis spectra of the complexes in methanol and DMSO were carried out by using Beckman DU 640 spectrophotometer. The IR spectra within 4,000–500 cm^{-1} region were made in KBr pellets on FT-IR PARAGON-1000 spectrophotometer (Perkin–Elmer). ^{1}H NMR spectra were recorded with Breuker AMX 300 MHz instrument. Measurements of the magnetic properties of the complexes were carried out in the solid state with a Quantum Desigon SQUID magnetometer (type MPMS-5) in the temperature range from 1.8–300 K. The effective magnetic moments were calculated using the formula:

$$\mu_{\mathrm{eff}} = 2.83(\chi_{\mathrm{M}} - \mathrm{T})^{1/2}\ \mathrm{B.M.},$$

where: χ_{M} - magnetic susceptibility of the appropriate lanthanide with an allowance for diamagnetism [14], T - temperature in K.

Results and discussion

Novel, solid amorphous compounds of Tb(III), Ho(III), Er(III) and Yb(III) with chrysin were synthesized. Based on elemental analysis, thermogravimetric studies and spectrophotometric determination of metal ions, the following molecular formula of the compounds were obtained: $Ln(C_{15}H_9O_4)_3 \cdot 4H_2O$ (where Ln = Tb(III),

Table 1 Results of elementary analysis of chrysin and its complexes with Tb(III), Ho(III), Er(III) and Yb(III)

Compound	M/%		C/%		H/%		Yield/%
	Obtained	Calculated	Obtained	Calculated	Obtained	Calculated	
$Tb(C_{15}H_9O_4)_3 \cdot 4H_2O$	16.14	16.04	54.46	54.56	3.46	3.56	46.4
$Ho(C_{15}H_9O_4)_3 \cdot 4H_2O$	16.63	16.55	54.20	54.23	3.38	3.54	54.2
$Er(C_{15}H_9O_4)_3 \cdot 4H_2O$	16.72	16.74	53.98	54.10	3.33	3.53	56.3
$Yb(C_{15}H_9O_4)_3 \cdot 4H_2O$	17.34	17.22	53.51	53.79	3.44	3.51	59.2

Table 2 Physical properties of the complexes

Compound	Solubility in MeOH/mol dm^{-3}	Conductivity/S cm^2 mol^{-1}		μ_{eff}/M.B.	
		DMSO	DMF	Obtained	Theoretical [15]
$Tb(C_{15}H_9O_4)_3 \cdot 4H_2O$	$1.76 \cdot 10^{-3}$	2.63	9.35	9.35	9.7
$Ho(C_{15}H_9O_4)_3 \cdot 4H_2O$	$1.60 \cdot 10^{-3}$	4.24	10.47	10.47	10.6
$Er(C_{15}H_9O_4)_3 \cdot 4H_2O$	$1.67 \cdot 10^{-3}$	1.87	9.33	9.33	9.6
$Yb(C_{15}H_9O_4)_3 \cdot 4H_2O$	$1.88 \cdot 10^{-3}$	2.10	4.38	4.38	4.5

Ho(III), Er(III), Yb(III)). Physical properties of the complexes are presented in Table 2. The complexes are stable in air and can be stored without change of composition. They are insoluble in most organic solvents except methanol, DMF and DMSO. In the latter solvent 10^{-3}–10^{-4} mol/dm^3 solutions could be prepared. Therefore the solid state chemistry methods for structural studies were applied. Low molar conductances for the complexes in DMSO and DMF correspond to non-electrolytes [16]. Complexes of Tb(III), Ho(III), Er(III) and Yb(III) with chrysin are paramagnetic. The values of the magnetic moments correspond to the number of unpaired electrons of free lanthanides ions. Hence, the oxidation state of metal ion in the complex does change and equals +3 [17, 18].

The thermal decomposition of chrysin and its complexes with lanthanide(III) ions were studied in nitrogen and air within 20–1,000 °C. The thermal decomposition of chrysin, in nitrogen atmosphere (Table 3), indicates that it undergoes one step mass changes (TG and DTG curves), with 100% mass loss, accompanied by two endothermic effects: I (onset 285.2 °C, enthalpy −36.65 kJ/mol) and II (onset 372.2 °C, enthalpy −47.56 kJ/mol) on the Heatflow curve. The process is completed at 433 °C. The phase transition peak in conventional DSC at 285 °C seems to be characteristic of melting point and occurs without mass loss in the TG curve [19]. The second endothermic effect corresponds to sublimation of chrysin molecules.

The results of the thermal analysis for the particular complexes (Table 3) of chrysin with lanthanide(III) ions provide the direct evidence that the studied compounds undergo multi-step changes. The common feature of these changes are two endothermic effects at the region of 25–185 and 173–282 °C. Those processes are corresponding to loss of water molecules. This fact suggests that part of water molecules may be coordinated to metal ions in complexes. The enthalpy values in kJ/mol corresponding to first endothermic effect are: −78.4, −92.8, −124.2, −58.2 and −2.5, −5.5, −4.3, −4.7 for second endothermic effect, respectively.

The thermogravimetric analysis shows that two solvate water molecules are quantitatively released from solids at temperatures around 89–98 °C, whereas remaining two water molecules, coordinated to metal ions Tb(III), Ho(III), Er(III) and Yb(III) complexes are released at range 244–248 °C [20]. The final products of the decomposition of complexes in nitrogen atmosphere are the lanthanide oxides and carbon [21].

Table 3 Thermal analytical data of the ligand and complexes (range 20–300 °C, nitrogen atmosphere)

Compound	Chrysin (L)		TbL3 4H$_2$O		HoL3 4H$_2$O		ErL3 4H$_2$O		YbL34H$_2$O	
	Stage I	Stage II	Stage I	Stage Ii	Stage I	Stage II	Stage I	Stage Ii	Stage I	Stage Ii
Temperature interval/°C	23–264	264–433	22–179	179–275	22–173	173–282	22–182	182–267	22–185	185–266
Mass losses/%	–	100	3.8	3.6	3.7	3.6	3.7	2.3	4.7	2.2
Heatflow:										
- Peak/°C	290	400	89	246	98	248	91	248	89	244
- Onset/°C	285	353	23	236	23	240	23	238	40	232
- Offset/°C	293	412	138	257	160	257	151	258	131	256
Enthalpy/J g^{-1}	−144.2	−187.1	−79.1	−2.5	−93.1	−5.5	−124.6	−4.3	−57.9	−4.7
Enthalpy/kJ mol^{-1}	−36.6	−47.6	−78.4	−2.5	−92.8	−5.5	−124.2	−4.3	−58.2	−4.7
Obtained mass losses H$_2$O/%	–	–	7.4	–	7.3	–	7.0	–	6.9	–
Calculated mass losses H$_2$O/%	–	–	7.27 (4H$_2$O)	–	7.23 (4H$_2$O)	–	7.21 (4H$_2$O)	–	7.17 (4H$_2$O)	–

The comparison of the DSC/TG data in nitrogen and air atmosphere for chrysin, reveals that the substance show different thermal behaviors. Thermal analysis of chrysin in air atmosphere indicates that it undergoes three-step conversion between 20–1,000 °C, accompanied by phase transformations and the carbonization effect (Heat flow curve). The first phase transition peak, endothermic effect (onset 284.7 °C) is the same in nitrogen atmosphere. The second and third stage are exothermic, marked on the Heat flow curve (onset: 395.9 and 496.4 °C) with 77.0% and 23.0% mass loss, respectively. The process is completed at 630 °C.

The final products of the decomposition of complexes in air atmosphere are the lanthanide oxides. The temperature of the oxide formation: Tb_4O_7, Ho_2O_3, Er_2O_3 and Yb_2O_3, changes irregularly in the lanthanide series from 715 to 760 °C.

The study of electronic spectra in ultraviolet and visible range for the complexes of lanthanide ions with chrysin was carried out in methanol and DMSO. The electronic spectrum of chrysin in methanol (experimental spectrum) within 200–700 nm has two intensive bands at $\lambda_{max} = 214$ and 270 nm; and a less intensive band at $\lambda_{max} = 316$ nm (Fig. 1). It is known that the band at 316 nm is related to the absorbance of the B ring (cinnamonyl system), whereas that at 269 nm is related to the A ring absorbance (benzoyl system). The spectra are consistent with the $\pi \rightarrow \pi^*$ transitions in a ligand molecule (Fig. 2).

A characteristic feature of the electronic spectra of the complexes of polyhydroxy-flavones with metal ions is the presence of new band (CT M ← L) in the visible range [22].

Examination of absorption spectra of Tb(III), Ho(III), Er(III) and Yb(III) complexes in methanol solutions indicate the new band centered at λ_{max} about 380 nm appears (Fig. 3). This new band, the maximum of which was estimated by standard Gaussian deconvolution is rather characteristic for 4C = O and 5C-OH chelation of the ligand [22–24].

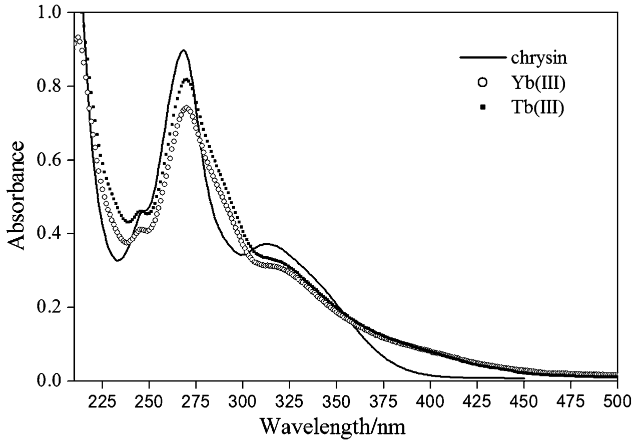

Fig. 1 Electronic absorption spectra of chrysin and complexes of Tb(III) and Yb(III) ions in methanol

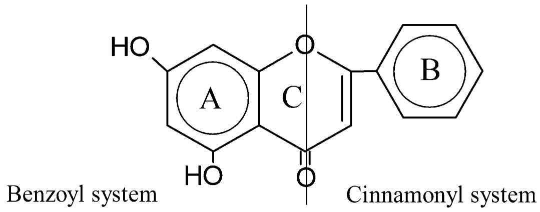

Fig. 2 Schematic formula of the molecule of chrysin

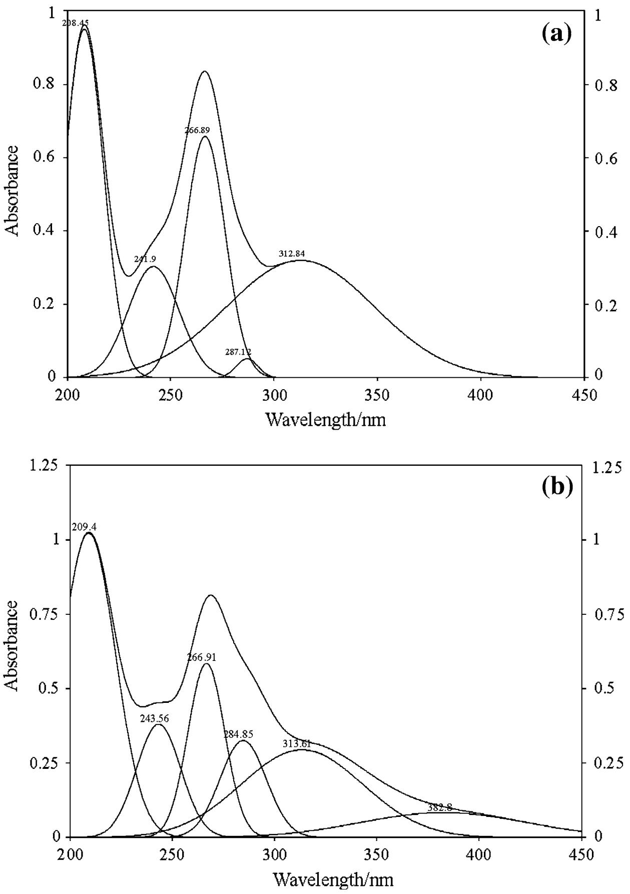

Fig. 3 Electronic absorption spectra of **a** chrysin and **b** Tb(III) complex with chrysin in methanol (Gaussian analysis)

The band intensity in the complexes increases considerably in comparison to the ligand itself. Molar absorption coefficients of the bands in the complexes are much higher than those in the ligand, which may be related to the change in the electronic density distribution.

In order to confirm the composition of the complexes and determine the metal-ligand coordination, the IR spectra of chrysin and its complexes with lanthanide(III) ions were recorded (Table 4). The IR spectra of the complexes are similar each to other and contain many absorption bands.

Table 4 Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) of chrysin and its complexes with lanthanide ions (300 K)

Compound	ν(O–H)	ν(C = O)	ν(C = C)			ν(C-OH)			ν(C–O–C)	
Chrysin (L)	3,090–2,550	1,653	1,612	1,577	1,556	1,363	1,356	1,188	1,168	1,245
$TbL_3 \cdot 4H_2O$	3,550–2,500	1,637	1,601	1,580	1,550	1,368	1,355	1,188	1,169	1,247
$HoL_3 \cdot 4H_2O$	3,550–2,500	1,636	1,603	1,580	1,552	1,370	1,356	1,188	1,169	1,248
$ErL_3 \cdot 4H_2O$	3,550–2,500	1,636	1,603	1,580	1,552	1,370	1,357	1,188	1,169	1,248
$YbL_3 \cdot 4H_2O$	3,550–2,500	1,636	1,602	1,580	1,552	1,368	1,357	1,188	1,169	1,247

In the IR spectrum of chrysin the valence vibrations of carbonyl group is coupled to oscillations giving the double band in the γ-benzopirone ring at 1,653 cm^{-1}, and absorption bands located at 1612, 1577 and 1556 cm^{-1} related to carbon vibrations in benzene and γ-piron rings (valance vibrations C = C). The ν(C–O–C) frequency and the ν_{ring}(C = C) changed slightly upon complexation indicating that the ring oxygen does not form metal-oxygen bonds with metal ion. Going from chrysin into its complexes with Tb(III), Ho(III), Er(III) and Yb(III) a shift of the carbonyl group (C = O) vibration from 1,653 to 1,636–1,637 cm^{-1} for the complexes may be observed. The shift can be explained by the fact that the group loses its original characteristics and participates in the binding of a metal ion via 4C = O and 5C–O^- oxygen donors after deprotonation to form the metal-oxygen bonds in the complexes [25]. The ν(O–H) frequency appears as a broad peak (from 2,550 to 3,550 cm^{-1}) indicating the existence of water, which is also coincident with results of thermal analysis. On the basis of spectral data we conclude that the structure of complexes is the same within the studied series of complexes. In the complexes of rare earths metal ions probably hydrogen bonds between inner and outersphere water molecules occur. These hydrogen bonds stabilize the structure of the complexes.

The ^{1}H NMR spectra of paramagnetic complexes cover broad region of chemical shift in case of Tb(III) (130 to −52 ppm) and Ho(III) (112 to −55 ppm) which could be anticipated based upon high value of S and L quantum numbers. For Tb(III) complex seven resonances at 130, 87, 64, 56, 46, −14, and −52 ppm and for Ho(III) complex also seven wide spread resonances at 111, 92, 46, 38, 35, −17, and −52 ppm are observed. In case of Er(III) complex different pattern of seven paramagnetically shifted resonances is observed; two resonances are shifted downfield to 21 and 15 ppm, while five others are shifted upfield to −3, −9, −15, −25, and −28 ppm. The most clear picture is obtained for Yb(III) complex, for which only two sharp resonances are found outside diamagnetic envelope, namely at 23 and −25 ppm, remaining five found within 12 to −4 ppm region, together with strong HDO and residual CHD_2 residual peak from DMSO-d_6. Although assignment of resonances could not been done even using correlation 2-D spectra due to short relaxation times of the protons in the complexes, the considerable isotropic shifts observed for two protons flanking the putative 4C = O and 5–O^- coordination sites is probably related to the strongest unpaired electron delocalization into 6C–H and 4C–H protons in case of Yb(III) complex. Seven paramagnetically shifted lines in all spectra is consistent with proposed structures, in which all chrysin anionic ligand are bound in the same way.

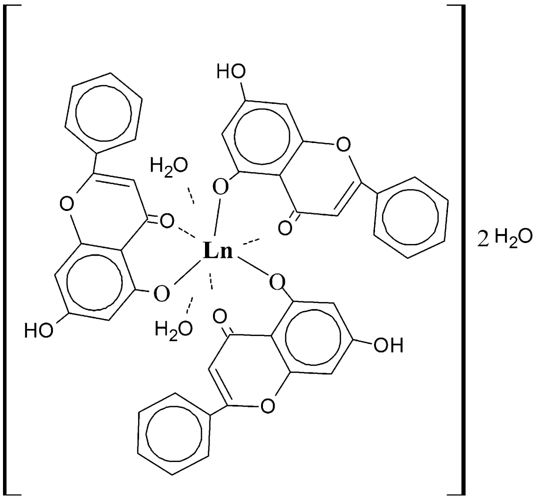

Fig. 4 Proposed structure of complexes of lanthanide ions with chrysin in solid state (Ln = Tb, Ho, Er, Yb)

Considering the stoichiometry of studied complexes, the number of first-sphere water molecules, estimated on basis of TG features and literature [10, 24], the following formulae of studied complexes have been deduced (Fig. 4).

Conclusion

This paper is devoted to the study of the synthesis, the structure and the physicochemical properties of the complexes of chrysin with Tb(III), Ho(III), Er(III) and Yb(III) ions. We found that in aqueous-methanol solutions and at pH 5.5–6, lanthanide(III) ions with chrysin form solid complexes of the following composition: $Ln(C_{15}H_9O_4)_3 \cdot 4H_2O$ where Ln is the cation of lanthanide. The oxidation state of metal ion in the complex does not change and equals +3. The results of the thermogravimetric analysis suggest that two water molecules are present in the inner coordination sphere of the complex and the two molecules are crystalline water.

On the basis of UV–vis, IR and ^{1}H NMR spectral data we conclude that in these complexes chrysin is chelated to the central metal ion *via* 4 = O and 5C–O oxygen donors.

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