Solid compounds of Ce(III), Pr(III), Nd(III), and Sm(III) ions with chrysin

J. Pusz · S. Wolowiec

Abstract New solid amorphous compounds of Ce(III), Pr(III), Nd(III), and Sm(III) with 5,7-dihydroxyflavone (L,chrysin) were obtained. Their composition and some physicochemical properties were studied by elementary analysis, thermogravimetric analysis, magnetic measurements, ^{1}H NMR, UV/Vis, and infrared spectroscopies. Upon heating, the hydrated compounds $[LnL_2(H_2O)_2Cl]\cdot 2H_2O$ decomposed to the oxides. Structure of the compounds was elucidated on the basis of obtained results. 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 natural products widely distributed in vegetables and currently consumed in large amounts in the daily diet [1, 2]. Over 4,000 of these compounds have been identified from both higher and lower plants and the list constantly expands.

The increasing interest in flavonoids is due to the appreciation of their broad pharmacological activity.

J. Pusz (✉)
Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, Rzeszow University of Technology, P.O. Box 85, 35959 Rzeszow, Poland
e-mail: jpusz@prz.edu.pl

S. Wolowiec
Department of Cosmetology, Faculty of Tourism and Health Sciences, University of Information Technology and Management, 2 Sucharskiego Str., 35-225 Rzeszow, Poland

Beneficial effects of flavonoids have been described for diabetes mellitus, cancer, allergy, viral infections, and inflammations. They can bind to biomolecules, such as hormone carriers and DNA, enzymes, catalyze electron transport, and scavenge free radicals [3–6]. In chemistry, flavonoids are used as colorimetric reagents for detection and determination of metal traces in solution [7]. Several reports are available in the literature on flavonoids and their metal complexes with non-transition and transition metal ions [8–27]. Chrysin (Fig. 1) is a flavone widely distributed in plants which was reported to have many biological activities including antibacterial [28], antioxidant [29], anti-inflammatory [30], antiallergic [31], anticancer [32], antiestrogenic [33], and anxiolytic acitivities [34].

Rare earth metals, which play vital roles in a vast number of widely differing biological processes, have not only physiological activities but also decreased toxicity after coordination with ligands [19, 20, 35–38].

Ansari has reported on lanthanide(III)–chrysin complexes [24]. The complexes Ln(chrysin)$_3$, (where Ln=La, Pr, Nd, Sm, Gd, Tb, and Ho) were synthesized in methanol solutions and found to be six-coordinate complexes. The absence of a water molecule in the coordination sphere was confirmed by the thermogravimetric study.

Zeng and co-workers has reported the complex of chrysin with lanthanum acetate [20]. The complex was synthesized in aqueous-ethanol solution and found to be an eight-coordinate where two molecules of chrysin and acetate ion and two molecules of water were attached to the La(III) ion in the inner coordination sphere.

In previous report [26], we investigated eight-coordinate complexes Ln(chrysin)$_3$·4H$_2$O. The thermogravimetric analysis shows that two water molecules are present in the inner coordination sphere of the complexes and two molecules are in the outer sphere.
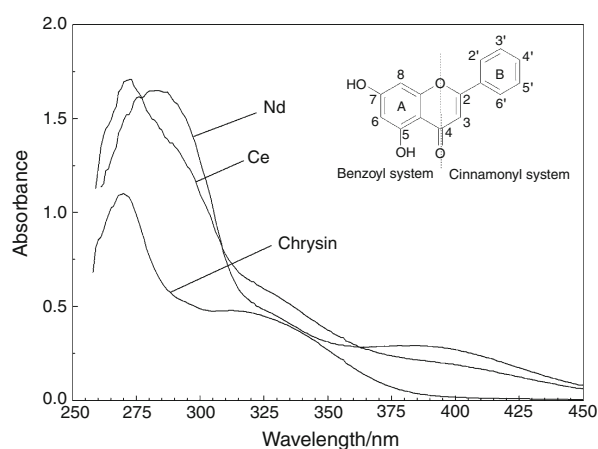
Fig. 1 UV–Vis spectra of chrysin-Ce(III) and chrysin-Nd(III) complexes in DMSO solution (*inset* shows molecular structure of chrysin)

In continuation of our study, here we report on complexes of trivalent lanthanides ions (Ce, Pr, Nd, Sm) with chrysin. We found a different composition depending on metal ion when the synthesis was carried out in methanol solutions. Elementary and thermogravimetric analyses were made to determine the composition of the compounds. The structure of complexes was deduced based on the results of visible and infrared as well as ^{1}H NMR spectroscopies.

Experimental

Materials

Lanthanide chlorides (99.9%:CeCl$_3$·7H$_2$O, PrCl$_3$·6H$_2$O, NdCl$_3$·6H$_2$O, SmCl$_3$·6H$_2$O, Sigma-Aldrich, USA), chrysin (99.9%, Sigma-Aldrich, USA), Na$_2$H$_2$edta·2H$_2$O (PPH POCH, Poland) were used in this study. All the other reagents: methanol, xylenol orange, arsenazo I, chloric(VII) acid, NaOH, dimethyloformamide (DMF), and dimethylsulfoxide (DMSO) were analytically pure.

Synthesis of the compounds

The complexes of chrysin with Ce(III), Pr(III), Nd(III), and Sm(III) were obtained by the same procedure. In a 250-mL

three-necked, round-bottomed flask equipped with electromagnetic stirrer was placed 140 mL methanol solution of chrysin (10 mmol). The mixture was then heated to 353 K and solid NaOH (6.25 mmol) was added. After 15 min, the solid hydrated lanthanide chloride (5 mmol) was added and mixture was boiled and stirred under reflux condenser for 10 h. After cooling, the solution was kept at room temperature for slow evaporation. The precipitates were formed, which were washed with copious amount of hot water–methanol (1:1) solution, separated by centrifuging, and dried in air at room temperature.

Instrumentation and measurement

The amounts of C and H in the investigated compounds were performed with an Elemental Analyzer EA 1108 apparatus (Carlo Erba). The metal content was determined spectrophotometrically with arsenazo I for La(III) and Ce(III) [39] and xylenol orange as indicator for Pr(III), Nd(III), and Sm(III) ions [40] in the samples were dissolved in chloric(VII) acid. In separate experiments, the metals were quantified by TG analysis. The final mass of the metal oxides obtained by heating the samples at 900 °C was recalculated for metal ion percentage. The water content was determined by gravimetric method and derivatography. The complexes were isolated as hydrated compounds [Ln(C$_{15}$H$_9$O$_4$)$_2$(H$_2$O)$_2$Cl]·2H$_2$O (where Ln = Ce, Pr, Nd, Sm). The results obtained are listed in Table 1.

Molar conductance at room temperature of the studied complexes was measured in 10^{-3} M DMSO and DMF solution using a CPC-551 type conductivity meter.

Measurements of magnetic susceptibility of the complexes Ce(III), Pr(III), Nd(III), and Sm(III) ions with chrysin were carried out in the solid state with a Quantum Desigon SQUID magnetometer (type MPMS-5) in the temperature range from 1.8 to 300 K. The effective magnetic moments were calculated using the formula:

$$\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2} \text{B.M.},$$

where χ_M is the magnetic susceptibility of the appropriate lanthanide with an allowance for diamagnetism [41], T is the temperature in K. For the investigated compounds, the

Table 1 Physical properties of lanthanide–chrysin(L) complexes

Complex	Found (Calc.)/%			Mol wt/g mol^{-1}	Solubility in MeOH/ mol dm^{-3}	Conductivity/ S cm^2 mol^{-1}	
	Ln	C	H			DMSO	DMF
[Ce(C$_{15}$H$_9$O$_4$)$_2$(H$_2$O)$_2$Cl]·2H$_2$O	18.87 (18.58)	47.95 (47.81)	3.47 (3.48)	753.02	5.25 × 10^{-3}	15.65	33.73
[Pr(C$_{15}$H$_9$O$_4$)$_2$(H$_2$O)$_2$Cl]·2H$_2$O	18.98 (18.69)	48.03 (47.74)	3.36 (3.47)	754.02	9.31 × 10^{-3}	15.75	35.25
[Nd(C$_{15}$H$_9$O$_4$)$_2$(H$_2$O)$_2$Cl]·2H$_2$O	19.26 (18.79)	47.71 (47.68)	3.35 (3.47)	755.02	1.10 × 10^{-2}	16.05	35.20
[Sm(C$_{15}$H$_9$O$_4$)$_2$(H$_2$O)$_2$Cl]·2H$_2$O	19.46 (19.86)	47.31 (47.06)	3.30 (3.42)	765.03	2.27 × 10^{-2}	15.35	34.45

Weiss constants (Θ) were calculated from the least squares fitting of the $1/\chi_M$ versus T curves. The Curie constants (C) were determined from $\chi_M \cdot T = f(T)$ dependence for $T = 300$ K. The values of effective magnetic moments and Curie and Weiss constants are listed in Table 2.

The thermal stability of the prepared compounds was determined using F.Paulik-J.Paulik-L.Erdey 3427 T derivatograph (MOM, Hungary). Measurements were made in air under the following conditions: $T = 25$–1000 °C, TG—100 mg, DTG—1/5, DTA—1/10, with 10°/min speed. To study dehydration process, measurements were made in air using TGA/DSC 1—thermogravimetric analyzer (Mettler-Toledo AG, Switzerland). The thermogravimetric results of

experiments for all studied compounds are collected in Table 3.

^{1}H NMR spectra, in DMSO-d_6, were obtained on a Bruker Avance II 500 spectrometer. The chemical shift data of chrysin and its complexes are listed in Table 4.

The UV/Vis and infrared spectra were taken with Beckman DU 640 and FT-IR NICOLET 6700 Thermo Scientific instruments. A study of the electronic absorption spectra in the ultraviolet and visible ranges for the obtained compounds with chrysin in methanol and DMSO were carried out. The UV/Vis and IR spectra of lanthanide-chrysin complexes are presented in Figs. 1 and 2, respectively. The results of infrared spectral examination of all

Table 2 The values of Curie constant (C), Weiss constant (Θ), and magnetic moments (μ_{eff}) for free lanthanide ions and for the investigated complexes

Ln	The value for isolated ions			Complexes of chrysin		
	$C_{theoret}$/cm^3 K mol^{-1}	$\mu_{eff.\ calc.}$/M.B.	$\mu_{eff.\ observed}$/M.B. [42]	$C_{theoret}$/cm^3 K mol^{-1}	Θ/K	μ_{eff}/M.B.
Ce	0.80	2.54	2.5	0.58	−6.39	2.39
Pr	1.94	3.58	3.5	1.22	−14.96	3.65
Nd	1.64	3.62	3.6	1.12	−23.88	3.32
Sm	–	0.84	1.5	–	–	1.72

Table 3 Thermoanalytical results (TG/DTG-DTA) for the complexes [LnL$_2$(H$_2$O)$_2$Cl]·2H$_2$O in air

Compound	T_1/°C	T_{endo}/°C	Total mass loss/%		Product of dehydration	T_2/°C	Residue mass/%		Final decomposition product
			Found	Calc.			Found	Calc.	
[CeL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	30–120		4.92	4.78	CeL$_2$(H$_2$O)$_2$Cl	220–670	23.40	22.83	CeO$_2$
	120–215	195	10.08	9.57	CeL$_2$Cl				
[PrL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	30–130		4.38	4.78	PrL$_2$(H$_2$O)$_2$Cl	230–860	23.11	22.58	Pr$_6$O$_{11}$
	130–225	175	9.98	9.56	PrL$_2$Cl				
[NdL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	30–130		4.49	4.77	NdL$_2$(H$_2$O)$_2$Cl	230–680	22.74	21.97	Nd$_2$O$_3$
	130–225	190	10.22	9.54	NdL$_2$Cl				
[SmL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	30–125		4.55	4.71	SmL$_2$(H$_2$O)$_2$Cl	290–730	23.38	23.00	Sm$_2$O$_3$
	130–190	170	9.76	9.42	SmL$_2$Cl				

$T_1(T_2)$—Temperature range corresponding to complex dehydration (decomposition), T_{endo}—Temperature of endothermic peak at DTA curve

Table 4 ^{1}H NMR chemical shift data for chrysin and complexes

Compound	Chemical shifts/δ, ppm						
	7-OH	5-OH	H-2′, 6′	H-3′, 4′, 5′	H-3	H-8	H-6
Chrysin [20]	12.83s	10.92s	8.07m	7.56–7.63m	6.97s	6.53s	6.23d
Ce	12.86[a]	n.obs.	7.6-8.3m	7.6–8.3m	9.01	6.26	12.89
Pr	17.67[a]	n.obs.	8.73[2H]	7.62[3H]	14.39	7.69	28.16
Nd	13.57[a]	n.obs	8.56[2H]	7.6–7.7[3H]	9.81	6.07	16.40
Sm	12.82[a]	n.obs	8.06	7.59	6.96	6.54	6.20

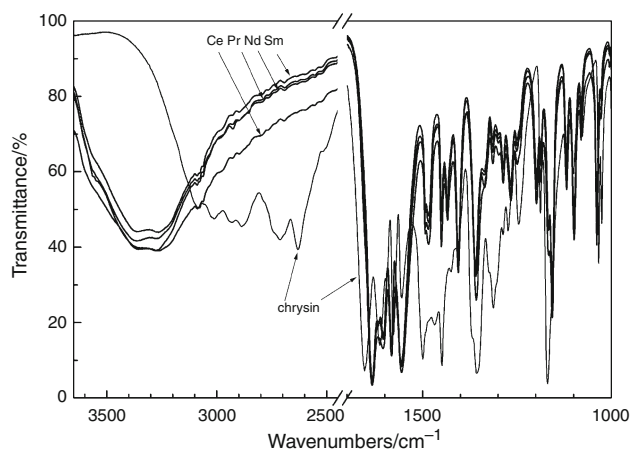[a] Disappear upon deuteration with D$_2$O

Fig. 2 IR absorption spectra of chrysin and its complexes with lanthanide ions in KBr

compounds in KBr pellets within 4,000–400 cm^{-1} region are listed in Table 5.

Results and discussion

In this article, we describe the synthesis of trivalent lanthanide (Ce, Pr, Nd, Sm) complexes with 5,7-dihydroxyflavone (chrysin, L). The complexes are characterized by thermogarvimetric analysis, UV-IR spectroscopic and

magnetic measurements. Elemental analysis of all of the complexes correlated well with the calculated values.

The obtained amorphous compounds are yellow (Ce, Pr, Nd) and orange (Sm); and have the empirical formula [Ln(chrysine)$_2$(H$_2$O)$_2$Cl]·2H$_2$O (where Ln = Ce, Pr, Nd, Sm), i.e., two chrysin molecules are bound to one metal ion.

The obtained complexes are stable in air and can be stored without change of composition. They are sparingly soluble in most polar organic solvents (methanol, DMF, and DMSO), but insoluble in non-polar solvents. The solubility of chrysin complexes in methanol at 293 K is of the order of 10^{-3} mol/dm^3 and increases within lanthanide series from Ce to Sm. Table 1 shows the analytical and molar conductance data for the complexes. Molar conductance values of the complexes measured in different solvents adequately confirm the nonelectrolytic nature of these metal chelates [43]. The complexes exhibited the 1:2 metal-to-ligand stoichiometry and can be formulated as [Ln(chrysine)$_2$(H$_2$O)$_2$Cl]·2H$_2$O (Ln = Ce, Pr, Nd, Sm), in which the ligand is coordinated to the metal ion after deprotonation of 5-OH group of chrysin molecule via 4-CO and 5-OH ring.

The complexes are paramagnetic. The values of the magnetic moments correspond to the number of unpaired electrons of free lanthanide ions. Thus, the oxidation state of metal ion in the complexes is +3. The deviation from the Curie–Weiss law at low temperature is consequence of

Table 5 Position of some bands^a (cm^{-1}) in IR absorption spectra of lanthanide(III)–chrysin complexes

Chrysin	Ce	Pr	Nd	Sm	Assignments
3100–2600 b, m	3675–2800 b, m	3675–2800 b, m	3675–2800 b, m	3675–2800 b, m	v(O–H), v(C–H)
1653 s	1633 s	1634 s	1634 s	1633 s	v(C=O)
1613 s,	1605 s,	1605 s	1604 s	1603 s	v(C=C)
1577 s,	1582 s	1582 s	1583 s	1582 s	
1555 s	1556 s	1556 s	1557 s	1557 s	
1448 s	1450 m	1450 m	1450 m	1450 m	δ(O–H) C–O–H
1356 s	1357 m	1358 m	1359 m	1360 m	v(C–O) C–C–O, C–O–C
1313 s	1313 m	1314 m	1313 m	1313 m	
1245 m	1249 m	1250 m	1250 m	1250 m	v(C–C) C–CO–C
1168 s	1165 m	1166 m	1165 m	1166 m	
1025 m	1027 w	1027 w	1027 w	1027 w	δ(O–H) in plane
908 m	911 w	911 w	911 w	910 w	δ(C–H) in plane
842 m	849 m	849 m	850 m	851 m	δ(C–C) in plane
807 m	803 m	804 m	804 m	804 m	δ(O–H) out of plane
782 m	780 w	780 w	780 w	780 w	δ(C–H) out of plane
746 m	745 w	745 w	745 w	747 w	
693 m	692 w	693 w	693 w	693 w	
642 m	638 m	638 m	639 m	639 m	δ(C–C) out of plane
511 m	506 m	505 m	506 m	508 m	
–	544 w	545 w	545 w	543 w	v(M–O)

^{a} *b* Broad, *m* medium, *s* strong, *w* weak

weak influence of the crystalline field on the central ions of the complexes. The bond of metal–ligand at the complexes is mainly electrostatic with slight covalence contribution [44, 45].

The UV–Vis absorption spectra of chrysin and their complexes were measured in methanol and DMSO within spectral range 200–700 nm and 250–700 nm, respectively. There are only two absorption bands observed in the absorption spectrum of free chrysin in methanol and DMSO. Two peaks at 313 nm (band I) and 267 nm (band II) in methanol, at 311 nm (band I) and 270 nm (band II) in DMSO are observed in the spectrum of chrysin (Fig. 1). Band I is considered to be associated with the absorption due to the B-ring portion (cinnamoyl system) and is related to the π–π* transitions within the aromatic ring of the ligand molecules, and band II is related to the absorption involving the A-ring portion (benzoyl system) which is due to π–π*, n–π*, and n–σ* transitions [16, 24, 46].

The electronic spectra of the methanol and DMSO solutions of the lanthanide(III) complexes with chrysin are similar. The characteristic feature of the spectra of Ce(III), Pr(III), Nd(III), and Sm(III) complexes is bathochromic shift of all the bands in comparison with free ligand spectrum, well-visible in difference spectra (not presented), see Table 6. Such bathochromic shifts of bands can be explained by complexation of the conjugated system. Due to the ligand band overlap, no inner 4f-5d or f–f-type transition bands can be observed.

The absorption band II shifted 3–9 nm in methanol and 3–15 nm in DMSO, compared to free chrysin (Table 6). This clearly indicates that ring A of benzoyl system is associated with metal ion. The presence of extra band of high intensity about 290–300 nm (well-visible in difference spectra) suggests that CH_3OH and DMSO molecules coordinate to the metal ion in complexes without displacing chrysin and increases the coordination number in

solution medium (non-electrolyte nature of the complexes in DMSO solution and methanol, which is weaker donor than DMSO) [9, 47, 48]. The change in spectra of the complexes demonstrates a change of symmetry of the field and effective geometry. The complexes spectra in methanol and DMSO revealed new broad bands at ∼380 and ∼385 nm, respectively. This broad band in visible region of the spectra of lanthanide ion complexes can be attributed to a weak, spin-forbidden f–f transitions of central metal ions, and/or CTML bands [21–23, 49]. Molar absorption coefficients of charge-transfer bands in the complexes are of the order of $1-2 \times 10^4$, i.e., are much higher than in the ligand, which may be related to the decrease of symmetry due to the change in the electronic density distribution.

^{1}H NMR spectral studies have been carried out to investigate the solution structure of the lanthanum chrysin complex and its stability in the solution medium. The ^{1}H NMR spectra of chrysin and its complexes with lanthanide ions have been recorded in DMSO-d_6. Assignments of proton signals of chrysin have been reported in [20, 24]. The ^{1}H chemical shifts are listed in Table 4. In case of the Pr(III) complex, the paramagnetic shifts are the largest. One of the O*H* resonances in the spectrum is missing. Another resonance of O*H* was identified by selective deuteration upon addition of D_2O into the sample of the complex in DMSO-d_6. The aromatic B proton resonance remain almost unaltered: ortho-proton 2′,6′-H signal of intensity [2H] is shifted downfiled of 0.64 ppm, while meta- and para-proton (3′,4′,5′) resonances [3H] remain unaltered. The singlets of intensity [1H] were attributed as follows: 7.69 ppm (8-H), 28.16 ppm (H-6), and 14.39 (H-3), which are paramagnetically downfield shifted by: 1.16, 21.93, and 7.42 ppm, respectively. In case of Nd(III) complex, the spectral picture is qualitatively the same, though the paramagnetic shifts are smaller. Accordingly, the resonance of 8-H (6.07 ppm) is slightly shifted upfield (−0.46 ppm), while the largest downfield paramagnetic shifts are again observed for H-6 (10.17 ppm), H-3 (2.84 ppm), and 7-O*H* (0.74 ppm). Praseodymium and neodymium are well known to induce upfield shifts, however, downloads shifts are also reported for these metal ions for the complexes of bbpy [50], substituted pyridines [51], and phen [52]. Accordingly to high values of magnetic moments of Pr(III) and Nd(III) complexes (see Table 2), the large paramagnetic shifts were expected. The large paramagnetic shifts of H-6 and H-2 and simultaneously smaller paramagnetic shifts for H-8 clearly indicate the involvement of 5-OH 4 C=O in coordination to these metal ions. The absence of 5-O*H* resonance indicates also that 5-O⁻/4-C=O is the chelating binding site of chrysin in Pr(III) and Nd(III) complexes.

In case of Ce(III) and Sm(III) complexes, the ^{1}H NMR picture is somewhat more complicated; the resonances of

Table 6 UV–Vis data ligands and complexes

Compound	Band I	Band II	Band III
MeOH			
$C_{15}H_{10}O_4$ (chrysin, L)	313	267	–
[CeL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	316	270	∼380
[PrL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	314	275	∼380
[NdL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	315	276	∼380
[SmL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	314	271	∼380
DMSO			
$C_{15}H_{10}O_4$ (chrysin, L)	311	270	–
[CeL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	Merged	273	∼380
[PrL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	Merged	285	385
[NdL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	Merged	284	384
[SmL$_2$(H$_2$O)$_2$Cl]·2H$_2$O	Merged	273	∼380

free chrysin as well as slightly shifted, paramagnetically broadened resonances are observed in DMSO-d_6 solutions. Nevertheless, for Ce(III) complex the largest paramagnetic shift follow the general trend observed previously for Pr(III) and Nd(III) complexes, namely the largest shift are observed for 6-H (6.60 ppm) and 8-H (2.04 ppm) protons. In case of Sm(III) complex, three additional resonances at: 6.20, 6.54, and 6.96 ppm are observed together with set of free chrysin resonances. Obviously, the complex dissociates in coordinating solvents, like DMSO used for the ^{1}H NMR studies. The chemical shift of protons remain unchanged when compared to free chrysin, and only slight paramagnetic broadening is observed.

The UV–Vis spectra also suggest that DMSO is strongly coordinating solvent in case of studied complexes [23–28]. The absorption bands of Ce(III) and Sm(III) complexes are unshifted in comparison with chrysin (Fig. 1).

In order to determine the structure of the obtained complexes in solid state, their IR absorption spectra were recorded in the region 4,000–400 cm^{-1}. All the study compounds of rare earth elements show similar structures in the solid state, Fig. 2. Table 5 shows the position most important IR bands of chrysin and its complexes with lanthanides(III) ions. IR spectra of the ligand and the complexes present evidence of coordination between the lanthanide(III) metal ions and chrysin. Specifically, in the IR spectrum of lanthanum complexes, the C=O stretching band was more shifted to a lower frequency in comparison to chrysin. Frequency of the ligand carbonyl group 1,653 cm^{-1} decreased 19–20 cm^{-1} in the complexes suggesting coordination of the carbonyl oxygen with the

Ln(III) ion. Bands due to the metal–oxygen bond appear at 543–545 cm^{-1} for all complexes [53, 54]. The bands typical for the aromatic ring vibrations are marginally shifted in the complexes compared to the respective bands in chrysin, which indicates that Ln(III) ions only weakly influence the benzene ring. The v(C–O–C) frequency changed slightly upon complexation, indicating that the ring oxygen does not form metal–oxygen bonds with central ion. All the infrared spectra of the studied complexes are characterized by broad band in the region 3,675–2,800 cm^{-1} due to presence of stretching vibrations, v_{OH} of hydroxyl group in hydrogen bonded water molecules, which corroborate with the results of the thermal analysis.

Thermal analysis by TG-DTA technique was proved to be very useful in determining the crystal water content in the complexes and their thermal stability and decomposition mode under controlled heating rate. The measurements were taken in air within 25–1,000 °C. The investigated lanthanide(III)–chrysin complexes are stable up to about 30 °C. Analysis of the DTA, DTG, and TG curves of the complexes investigated demonstrate that they undergo gradual decomposition which increase in temperature (Fig. 3). For all the investigated complexes, the thermal decomposition mode seems to follow the same model. The scheme of compounds decomposition consist of two general steps. The first one is related to dehydration process whereas the second stage is related with degradation of anhydrous complexes. The shape of TG and DTG curves and endothermic effects in the DTA curves indicate that some water molecules are present in the chrysin complexes

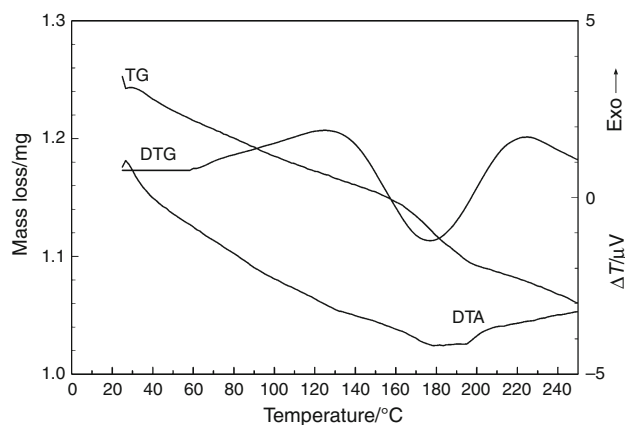**Fig. 3** TG/DTG-DTA curves for the chrysin complexes with **a** Pr(III) and **b** Sm(III) ion in air
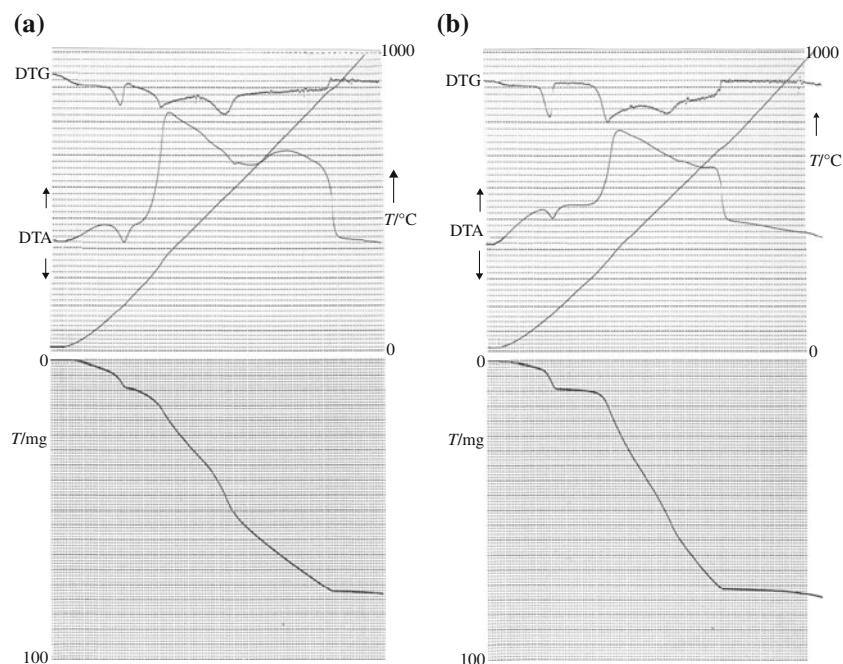
Fig. 4 TG/DTG-DTA curves of dehydration of [PrL₂(H₂O)₂Cl]·2H₂O

of Ce(III), Pr(III), Nd(III), and Sm(III) ions. They dehydrate within the temperature range 30–230 °C, losing all water of complexes. The dehydration process of chrysin complexes occurs in two steps (Fig. 4; Table 3). The first step at range 30–130 °C is connected with loss of two water molecules. This process is accompanied by very weak endothermic peak at about 75 °C, which is not detected able by used DTA thermocouple. Further heating of compounds resulting in removing of next two water molecules. This step corresponds to endothermic effect at about 180 °C. Stepwise dehydration process illustrates different mode of water molecules bonding. It can be concluded that at the first stage of complexes dehydration corresponds to release of two weakly bonded water molecules. Probably, these molecules occupy position outside coordination sphere of lanthanide ions being hydrogen bonded with flavonoid ligand. The water molecules removed in the second step of dehydration are more tightly bonded and they are released in significantly higher temperature. It is assumed that these two water molecules are probably directly bonded to lanthanide ions in inner coordination sphere, completing the coordination number of the metal ion. Similar effect were obtained earlier for the complexes of other lanthanides ions with some polihydroksyflavones and their derivatives [20–23].

As the result of dehydration process, anhydrous compounds of chrysin are formed. The anhydrous compounds are unstable upon heating, and decompose suddenly with a mass loss observed on the TG curves. Only anhydrous complex of samarium(III) demonstrates stability in the temperature range 190–290 °C (Table 3). This stage of decomposition is accompanied by a complex exothermic effect on the DTA curve in the temperature range 230–860 °C, suggesting that rather oxidation of the sample takes place along with the decomposition. The final products of the decomposition of lanthanide(III) chrysin complexes are suitable metal oxides: CeO_2, Pr_6O_{11}, Nd_2O_3, and
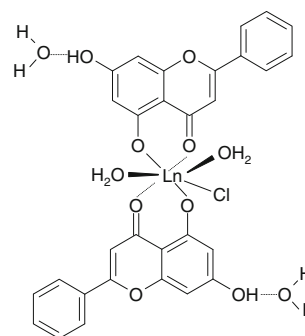

Fig. 5 Proposed structure of [LnL₂(H₂O)₂Cl]·2H₂O complexes
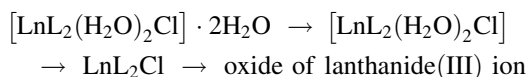
Sm_2O_3. The temperature of the oxide formation changes irregularly in the lanthanide series from 670 to 860 °C.

The scheme of thermal decomposition: hydrated complex → anhydrous complex → oxide is very characteristic of lanthanide organic complexes and it was observed by many authors [55–57].

Based upon large downfield paramagnetic shifts of H-6 and H-3 resonances in the ^{1}H NMR spectra of the complexes, the remarkable shifts of 4 (C=O) stretching vibrations in the IR spectra of solid complexes, and thermogravimetric monitoring of hydrates studied here the structure of the complexes obtained in this study can be represented by following formula (Fig. 5).

Conclusions

This study contributes to a better elucidation of the chelation chemistry of flavonoids with lanthanide ions. The IR and NMR data of the complexes indicate that the chrysin molecule coordinates to metal via the ring 4-oxo and deporotonated 5-O⁻ group. In air atmosphere, complexes decompose in the two steps, loosing water molecules and finally they undergo degradation and combustion of organic ligand. The scheme of water release is as follows:

$$\left[LnL_2(H_2O)_2Cl\right] \cdot 2H_2O \ \rightarrow \ \left[LnL_2(H_2O)_2Cl\right]$$
$$\rightarrow \ LnL_2Cl \ \rightarrow \ oxide\ of\ lanthanide(III)\ ion$$

Based on spectral and thermogravimetric data, it is proposed that aquachloro complexes of chrysin with lanthanide ions are seven coordinate in solid state.

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