INVESTIGATION OF SOME PHYSICOCHEMICAL PROPERTIES OF 4-NITROCINNAMATES OF LANTHANIDES(III)

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ABSTRACT

Lanthanide(III) 4-nitrocinnamates were synthesized as polycrystalline hydrated solids with the general formulae: $Ln(C_9H_6NO_4)_3 \cdot nH_2O$ (where Ln = lanthanons (without Ce(III)), n=1 for La, Pr-Tb and n=2 for Dy-Lu). The complexes were characterized by elemental analysis, FTIR spectroscopy, magnetic and thermogravimetric studies and also by X-ray diffraction (XRD) measurements. The carboxylate groups bind as bidentate chelating. On heating to 1173 K in air all compounds at first dehydrate in one stage to form anhydrous salts, that next with rising temperature are being directly decomposed (complexes of Pr(III) and Eu(III)) or with the intermediate formation of oxycarbonates (the rest of analysed compounds) to the oxides of respective metals. The gaseous products of compound thermal decomposition in nitrogen were also determined. The magnetic susceptibilities were measured over the ranges 76-303 K and 1.8-303 K, and their magnetic moments were calculated. The results show that 4-nitrocinnamates of lanthanides(III) are high-spin complexes with weak ligand field.

Keywords: lanthanides, complexes, thermal stability, magnetic properties, 4-nitrocinnamates

INTRODUCTION

Cinnamic acid (3-phenyl-2-propenoic acid) as a phenyl alanine forms a relatively large family of organic isomers.[1,2] It possesses antibacterial, antifungal and parasite fighting abilities. Its derivatives are important metabolic building blocks in the production of lignins for higher plants, and some of them are important pharmaceutics for high blood pressure and stroke preservation and possess antitumour activity. With flavonoids in vine they create pigments and tannin agents that give each vintage its characteristic bouquet and colour. Some of its derivatives may be also used as sunscreens.[3] In the molecule of cinnamic acid and its derivatives the carboxylic group being separated from the aromatic ring by a double bond causes the conjugations between the –C=C– bond and P electron system. Therefore cinnamic acid and its derivatives are extensively studied.[1,2]

Lanthanide ion complexes attract considerable attention in last decades since that may be used in biotechnology, bioengineering and medicine. Catalytic activity of carboxylates containing lanthanide ions for hydrolysis of nucleic acids is of particular interest.[4] The carboxylate chemistry has been applied to metallation and oxymetallation reactions. Transition metal carboxylates are used as catalysts in many industrial processes and as selective oxidizing agents in organic chemistry. They also play important role in inorganic and bioinorganic chemistry and in some areas of daily life.[5,6] Many of them are a component of several vitamins and drugs.[7] They serve for the biomedical material productions and the therapeutic agents being used in anti- cancer therapy. Carboxylic acids are applied for absorbing, preserving and separating many gases and their complexes with 4f electron elements having the luminescence properties find application in optical and electronic industries.[8] They play significant role in crystal engineering and serve for paramagnetic organic material productions.[9-11] Their compounds form interesting group of single – molecule magnets (SMMs) that exhibit magnetization hysteresis at low temperature (yielding the special property of macroscopic magnets).

From the survey of literature it follows that the complexes of lanthanides(III) with 4-nitrocinnamic acid have not been obtained and studied so far. Therefore as a continuation of our studies on carboxylates of transition metal ions we decided to synthesize them and to examine some of their properties such as thermal stability in air at 293-1173 K, magnetic properties in the range of 77-303 K and 1.8-300 K and to record their FTIR spectra. 4-Nitrocinnamic acid is a white or yellow solid sparingly soluble in water. Its melting point temperature is equal to 200°C. For preparation of lanthanide(III) complexes we used its ammonium salt easily soluble in water.

EXPERIMENTAL

Chemical and instruments

All chemicals and solvents used for the synthesis were of commercially available reagent grade and used without purifications. 4-Nitrocinnamate of ammonium (pH~5) of 0.1 mol L^{-1} concentration was prepared by the addition of NH_3 (aq) solution (25 % pure, Polish Chemical Reagents in Gliwice (Poland)) to 4-nitrocinnamic acid in water solution (99 % solution Aldrich Chemical Company). In order to obtain the lanthanide(III) chlorides the samples of 0.8 g of lanthanide oxides (99.9% pure, Aldrich Chemical Company) were digested in the equivalent amounts of concentrated HCl (35-38% pure, Polish Chemical Reagents in Gliwice (Poland)). The solutions were constantly heated. The lanthanide(III) chlorides were practically evaporated to dryness. The residue was dissolved in water forming the solutions of lanthanide(III) chlorides, the concentration of which was equal to 0.1 mol L^{-1} and pH ~ 5.

The contents of carbon, hydrogen and nitrogen in complexes were determined by elemental analysis using a CHN 2400 Perkin–Elmer analyser. The amounts of M(III) metals were established by X-ray fluorescence XRF method using spectrophotometer of X-ray fluorescence with energy dispersion ED XRF–1510 (Canberra-Packard).

The FTIR spectra of complexes, 4-nitrocinnamic acid, its salt with Na and the products of the final complex decompositions were recorded over the range of 4000–400 cm^{-1} using an M–80 Perkin–Elmer spectrometer. The samples were prepared as KBr discs.

The X-ray diffraction patterns of compounds and the products of decomposition process were taken on a HZG-4 (Carl –Zeiss, Jena) diffractometer using Ni filtered CuK_a radiation. The measurements were made within the range of $2\theta = 4$–80° by means of Bragg-Brentano method.

The thermal stability and decomposition process of complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow in the temperature range of 297–1173 K at a heating rate of 5 $K \cdot min^{-1}$. The initial mass of samples of 4-nitrocinnamates of lanthanides(III) used for measurements changed from 4.45 to 6.61 mg. Samples of these compounds were heated in Al_2O_3 crucibles.

The gaseous products of thermal decomposition of analysed complexes were also identified with TG-FTIR technique using TGA Q 5000 instrument (Firm TA Instruments) with Nicolet 6700 Spectrophotometer. The measurements were carried out in Pt crucibles under nitrogen flow 25mL·min^{-1} in the range of 297–1173 K at a heating rate of 10 $K \cdot min^{-1}$. The initial masses of samples used for measurements changed from 7.87 to 8.26 mg.

Magnetic susceptibilities of polycrystalline samples of 4-nitrocinnamtes of lanthanons(III) were investigated at 77–303 K and additionally for Gd(III) complex at 1.8–303 K. The measurements were carried out using the Gouy's method and with the use of Quantum Design SQUID-VSM magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 7 T. Measurement samples of compounds were made at magnetic field 0.1 T. The SQUID magnetometer was calibrated with the palladium rod sample. In the case of Gouy's method the mass changes were obtained from Cahn RM-2 electrobalance. The calibrate employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5}$ cm^3 g^{-1}. The measurements were made at a magnetic field strength of 0.99 T. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants.[9,12]

The effective magnetic moment values were calculated from the equation:

$$\mu_{eff} = 2.83 \, (\chi_M \times T)^{1/2}$$

where: μ_{eff} - effective magnetic moment, χ_M – magnetic susceptibility per molecule and T - absolute temperature

Synthesis

The 4-nitrocinnamates of lanthanons(III) were prepared by adding the equivalent quantities of 0.1 molL⁻¹ ammonium 4-nitrocinnamate (pH~5) to a hot solution of lanthanide(III) chlorides and crystallizing at 293 K. For the reach of equilibrium state the solids were heated for 1 h at 333-343 K with constant stirring. Next they were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass.

The 4-nitrocinnamate of Na was prepared by the addition of equivalent amount of 0.1 molL⁻¹ ammonium 4-nitrocinnamate to NaOH solution containing 0.1 g NaOH (analytically pure, Polish Chemical Reagents in Gliwice (Poland)) and crystallizing.

RESULTS AND DISCUSSION

4-Nitrocinnamates of lanthanides(III) were synthesized as polycrystalline products of general formulae: $Ln(C_9H_6NO_4)_3 \cdot nH_2O$ (where Ln = lanthanons (without Ce), n=1 for La, Pr-Tb and n=2 for Dy-Lu) (Table 1).

Table 1. Elemental analysis data for lanthanide(III) 4-nitrocinnamates.

Complex	C / %		H / %		N / %		M / %	
L = $C_9H_6O_4N$	calcd.	found	calcd.	calcd.	calcd.	found	calcd.	found
$LaL_3 \cdot H_2O$	44.20	44.10	2.72	2.68	5.73	5.60	18.95	19.23
$PrL_3 \cdot H_2O$	44.08	43.98	2.72	2.58	5.71	5.70	19.17	18.94
$NdL_3 \cdot H_2O$	43.89	43.69	2.70	2.64	5.68	5.60	19.53	18.75
$SmL_3 \cdot H_2O$	43.52	43.48	2.68	2.60	5.64	5.60	20.20	20.25
$EuL_3 \cdot H_2O$	43.43	43.22	2.41	2.38	5.63	5.58	20.37	20.37
$GdL_3 \cdot H_2O$	43.13	43.10	2.66	2.46	5.59	5.49	20.92	20.95
$TbL_3 \cdot H_2O$	43.03	43.00	2.65	2.48	5.57	5.48	21.10	21.00
$DyL_3 \cdot 2H_2O$	41.83	41.46	2.84	2.64	5.42	5.40	20.98	20.19
$HoL_3 \cdot 2H_2O$	41.70	41.40	2.83	2.63	5.40	5.40	21.22	21.19
$ErL_3 \cdot 2H_2O$	41.58	41.40	2.82	2.68	5.39	5.30	21.45	20.69
$TmL_3 \cdot 2H_2O$	41.48	41.38	2.81	2.61	5.37	5.30	21.63	20.74
$YbL_3 \cdot 2H_2O$	42.24	42.20	2.86	2.68	5.47	5.42	22.55	22.00
$LuL_3 \cdot 2H_2O$	41.17	41.08	2.79	2.59	5.33	5.30	22.23	22.13

Their colour are typical for Ln(III), which is connected with the similar electron density in the complexes. In their molecules the f–f electronic transitions of the metal ions are those of the lowest energy and absorption occurs at relatively high wavelengths, depending on the nature of the metal ion.[13]

Infrared spectra

4-Nitrocinnamates of Ln(III) show similar solid state FTIR spectra. The band at 1688 cm⁻¹ originating from the RCOOH group, presented in the acid spectrum is replaced in the spectra of complexes by two bands at 1600–1596 cm⁻¹ and 1428–1416 cm⁻¹, which can be ascribed to the asymmetric and symmetric vibration of COO⁻ group, respectively.[14-22] The bands with the maxima at 3568–3420 cm⁻¹ characteristic for v(OH) vibrations confirm the presence of crystallization water molecules in the complexes. The bands of -C=C- vibrations are observed at 1648-1640 cm⁻¹. The bands of v(C=C) ring vibrations appear at 1584–1544 cm⁻¹, 1248-1108 cm⁻¹. The valency v(C-N) vibration bands occur at 872-868 cm⁻¹. The bands at 1516–1512 cm⁻¹ and 1384-1344 cm⁻¹ are assigned to asymmetric and symmetric valency vibrations of NO_2 group. They are not significantly shifted with respect to those of the parent acid, and thus one must conclude that the NO_2 group is not coordinate to the metal ions. The bands at 836cm⁻¹ may be ascribed to C-H valency vibrations in the 1:4 substituted ring positions. The bands at 556–548 cm⁻¹ confirm the ionic metal-oxygen bond.[6,7] They change their position in the FTIR spectra which may suggest the different stability of metal-ligand bonding. In the FTIR spectra of the complexes the bands of $v_{as}(OCO)$ are shifted to the lower frequencies whereas the bands of $v_s(OCO)$ are moved to higher ones compared to those of the sodium salt (Table 2). Therefore it is possible to assume that the carboxylate ion is a bidentate, chelating group.[6,7,23-25]

Table 2. Wavenumbers (cm⁻¹) of OCO⁻ , NO_2, C–N and M–O bands in the FTIR spectra of 4-nitrocinnamates of lanthanides(III), Na and that of the COOH band in 4-nitrocinnamic acid.

Compound	v (C=O)	$v_{as}(OCO)$	$v_s(OCO)$	$\Delta v(OCO)$	$v_{as}(NO_2)$	$v_s(NO_2)$	$\Delta v(NO_2)$	$v(C–N)$	$v(M–O)$
L = $C_9H_6O_4N$									
$LaL_3 \cdot H_2O$	–	1596	1416	180	1512	1348	164	848	552
$PrL_3 \cdot H_2O$	–	1596	1416	180	1512	1348	164	848	548
$NdL_3 \cdot H_2O$	–	1596	1416	180	1512	1348	164	848	548
$SmL_3 \cdot H_2O$	–	1596	1416	180	1512	1348	164	848	552
$EuL_3 \cdot H_2O$	–	1596	1416	180	1512	1348	164	852	548
$GdL_3 \cdot H_2O$	–	1600	1420	180	1512	1344	168	852	552
$TbL_3 \cdot H_2O$	–	1600	1420	180	1512	1348	164	852	548
$DyL_3 \cdot 2H_2O$	–	1600	1420	180	1516	1348	168	852	548
$HoL_3 \cdot 2H_2O$	–	1600	1420	180	1516	1348	168	852	548
$ErL_3 \cdot 2H_2O$	–	1600	1420	180	1516	1348	168	848	548
$TmL_3 \cdot 2H_2O$	–	1600	1428	172	1516	1348	168	852	552
$YbL_3 \cdot 2H_2O$	–	1600	1420	180	1516	1348	168	852	556
$LuL_3 \cdot 2H_2O$	–	1600	1428	172	1516	1348	168	852	556
NaL	–	1610	1392	218	1512	1348	164	848	–
HL	1688	–	–	–	1512	1352	160	852	–

The structure of the carboxylate groups is bidentate chelating when the bands of v_{as}(OCO) and v_s(OCO) in analysed complex FTIR spectrum are shifted to lower and higher wavenumbers compared to those for sodium salt; or Δv(OCO) of studied complex $\ll\Delta v$(OCO) of sodium salt. Bidentate bridging structure exists when bands of v_{as}(OCO) and v_s(OCO) in studied FTIR spectrum complex are shifted to higher wavenumbers, compared to those for sodium salt; or Δv(OCO) of studied complex $\gg\Delta v$(OCO) of sodium salt. For monodentate geometry of carboxylate group the bands of v_{as}(OCO)and v_s(OCO) in analysed FTIR spectrum compound are moved to higher and lower wavenumbers, respectively, compared to those for sodium salt; or Δv(OCO) of studied complex $\gg\Delta v$(OCO) of sodium salt.[6,7,20,23,24]

The magnitudes of separations, ΔvOCO between the frequencies due to v_{as}(OCO) and v_s(OCO) in the analysed complexes indicate a lower degree of ionic bond in these compounds compared to that in sodium salt.

In order to verify that prepared complexes are not converted to the nitrite isomers (during precipitation or on heating to 533 K) the FTIR spectra of the hydrates of 4-nitrocinnamates, and of dehydrated complexes, and also of sodium nitrate were recorded. A survey of the literature shows that under the influence of sunlight or with rising the temperature the nitro complexes may be transformed to the nitrite analogues in the endothermic process.[26] It was found that isomerisation of the nitro group may accompany the dehydration process of the complex or be connected with the transformation process in its inner sphere. As a monodentate ligand, nitrite ion may be bounded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrite complex. The general effect of coordination via nitrogen is a rise in the frequencies of both v_{as}(NO$_2$) and v_s(NO$_2$) compared to the values for the free ion ~1328cm^{-1} and ~1260cm^{-1}, respectively.[6,7,24] The FTIR spectra recorded for the hydrated and dehydrated 4-nitrocinnamates of lanthanides(III) show that the nitro group is not transformed to the nitrite group with rising temperature. No bands confirming he isomerisation of the nitro group through the oxygen atom are observed.

X-ray powder diffraction

The X-ray diffraction pattern analysis reveals that 4-nitrocinnamates of lanthanides(III) are crystalline compounds (Fig. 1).
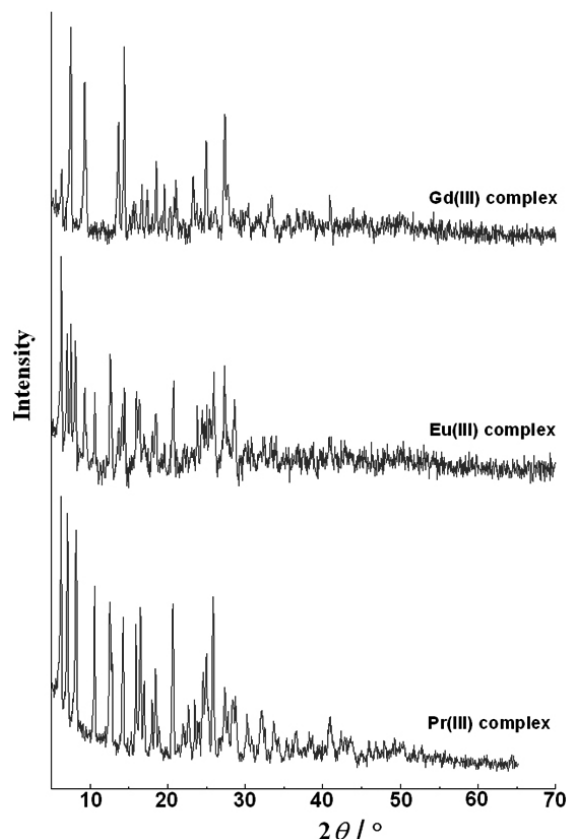

In the series of 4-nitrocinnamates of La(III), Pr(III), Nd(III), Sm(III) and Eu(III) the most intense peaks appear at the 2θ angles: 6.3; 7.0, 8.2, 14.2, 16.5, 25.8 and 28.9 while in the case of those for heavy lanthanides(III) they are at the angles: 6.3; 7.5, 10.2, 13.50, 14.3, 16.2, 25.5 similarly as those determined for 4-chloro-2methoxybenzoates of heavy lanthanides(III) and yttrium.[27]

Thermal analysis

The thermogravimetric studies of 4-nitrocinnamates of lanthanides(III) were carried out in air in the temperature range of 293–1173 K (Table 3, Fig. 2). TG, DTG and DSC curves were recorded using DSC/TG technique. When heated to 1173 K the complexes decompose in two or three steps. They are stable up to 323–441 K. Next in the range of 323–452 K all 4-nitrocinnamates dehydrate in one step with endothermic peaks (DSC curves) losing one or two molecules of water and form anhydrous compounds.
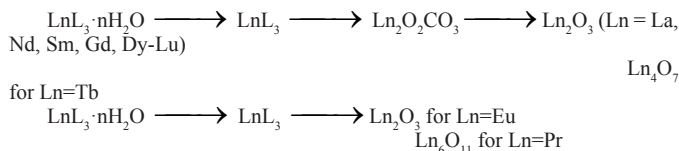
ΔT_1 – temperature range of dehydration process, n – number of water molecules lost in the one step, ΔT_2 – temperature range of anhydrous complex decomposition, T_k – final temperature of decomposition process, ΔH^* – enthalpy value for one molecule of water

The mass losses calculated from TG curves being equal to 1.80-4.63 % correspond to the loss of 1 or 2 molecules of water (theoretical values 2.39-4.69 %). From the temperature data of dehydration process it follows that La(III) complex is the most thermally stable compound while those of Tm(III), Yb(III) and Lu(III) the least ones in the group of analysed 4-nitrocinnamates of lanthanides(III). The energetic effects accompanying the dehydration processes were also determined. The enthalpy values, ΔH, change from 94.20-32.04 kJ·mol^{-1} and 56.00-29.25 kJ·mol^{-1} per one molecule of water. These values indicate that the water molecules are coordinated to the central ions with different strengths depending on their positions in the complex coordination spheres.

The anhydrous complexes of lanthanides(III) in their second step of decomposition (with the exception of Pr(III) and Eu(III) form oxycarbonates being the intermediate products that step by step release gradually the parts of ligands (551–794 K) and form the oxides of appropriate metals. The mass losses calculated from TG curves are equal to 59.10 and 73.80 % indicating the oxycarbonate formations (theoretical values are 61.20 and 74.40 %). In the third stage of their decomposition the intermediate products, Ln$_2$O$_2$CO$_3$, decomposed to the oxides of respective metals: Ln$_2$O$_3$ (where Ln = La, Nd, Sm, Gd, Dy-Lu) and Tb$_4$O$_7$. The final temperature values of their formation are in the range of 973–1073 K. The mass of residue determined from TG curves are 21.80% and 26.00 % (theoretical 22.20% and 25.70 %).
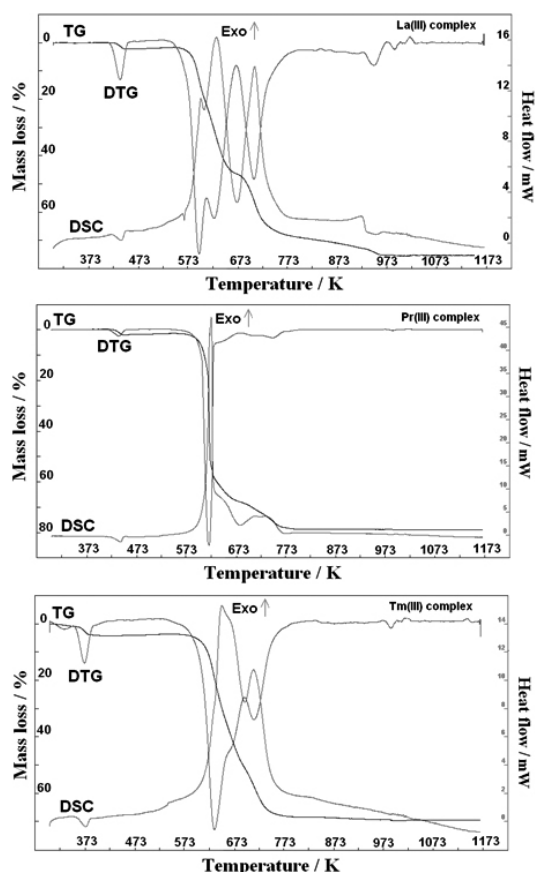
The anhydrous 4-nitrocinnamates of Pr(III) and Eu(III) are directly decomposed to Pr$_6$O$_{11}$ and Eu$_2$O$_3$ in the range of 540–790 K. The found masses of residue are equal to 19.50% and 23.40 % (theoretically calculated values are 18.90% and 23.40 %). The final products of decomposition obtained as oxide metals were verified by comparing their FTIR spectra and powder diffractograms with those of pure oxide.

The results indicate that the thermal decomposition of 4-nitrocinnamates of lanthanides(III) in air proceeds in the following way:

$$LnL_3 \cdot nH_2O \longrightarrow LnL_3 \longrightarrow Ln_2O_2CO_3 \longrightarrow Ln_2O_3 \ (Ln = La,$$
Nd, Sm, Gd, Dy-Lu)

$$Ln_4O_7$$

for Ln=Tb

$$LnL_3 \cdot nH_2O \longrightarrow LnL_3 \longrightarrow Ln_2O_3 \ for \ Ln=Eu$$
$$Ln_6O_{11} \ for \ Ln=Pr$$

From the obtained data it appears that coordination numbers of central ions is probably equal to 7 or 8. The molecules of water seem to be coordinated with central ions and released in the low temperature.[28,29] The data obtained from the determination of the complete structures of these complexes can give the fair information on the positions of water molecules in the compounds, but their single crystals have not been synthesized so far. However the attempts to obtain them have been still made.

The gaseous products released during complex decompositions (Fig. 3) reveal them to be the molecules of H$_2$O, CO, CO$_2$, NH$_3$ and hydrocarbons.

Fig. 1. X-ray diffraction patterns of 4-nitrocinnamates of Pr(III), Eu(III) and Gd(III).

Fig. 3. FTIR spectra of gaseous products for Nd(III) 4-nitrocinnamate decomposition in N_2 at 568 K.

The FTIR spectra were recorded. For all analysed complex decompositions the bands at 4000–3500 cm^{-1} and 1700–1500 cm^{-1} (323–452 K) confirm the presence of H_2O molecules in the complexes. With rising temperature the bands at 2500–2250 cm^{-1} and 750–600 cm^{-1}, respectively result from CO_2 vibrations, whereas the bands observed at 2200–2000 cm^{-1} are characteristic for CO. The absorbance peak of methane appears around 3000 cm^{-1} and NH_3 around 1000 cm^{-1}.[30,31]

Magnetic properties

In order to estimate the nature of metal ligand bonding in analysed complexes and try to consider why their colours are typical for Ln(III) ions the magnetic susceptibility of 4-nitrocinnamates of lanthanides(III) was determined over the range of 77–303 K (Fig. 4).

Fig. 2. TG, DTG and DSC curves of La(III) Pr(III) and Tm(III) complexes in air atmosphere.

Table 3. Temperature ranges of thermal stability of lanthanide(III) 4-nitrocinnamate in air at 293–1173 K and enthalpy value. of dehydration process for analysed complexes.

	ΔT_1 / K	Mass loss / %		n	ΔT_2 / K	Mass loss / %		Residue mass / %		T_k / K	ΔH / (kJ·mol^{-1})	ΔH^* / (kJ·mol^{-1})
$L = C_9H_6O_4N$		calcd.	found			calcd.	found	calcd.	found			
LaL$_3$·H$_2$O	441-448	2.45	2.20	1	555-794	69.7	68.8	22.20	21.80	1023	56.00	–
PrL$_3$·H$_2$O	419-448	2.44	2.02	1	551-790	–	–	18.90	19.50	823	36.02	–
NdL$_3$·H$_2$O	412-452	2.43	2.49	1	565-783	73.6	72.1	22.80	22.00	1073	41.00	–
SmL$_3$·H$_2$O	405-430	2.41	2.00	1	573-673	61.2	59.1	23.40	23.30	962	44.20	–
EuL$_3$·H$_2$O	387-437	2.41	1.80	1	540-790	–	–	23.60	23.40	940	32.04	–
GdL$_3$·H$_2$O	387-401	2.39	2.40	1	558-697	72.1	72.3	24.10	23.90	990	45.00	–
TbL$_3$·H$_2$O	344-405	2.39	2.50	1	573-687	74.1	72.0	24.80	24.40	1005	42.80	–
DyL$_3$·2H$_2$O	333-373	4.64	4.23	2	573-783	74.4	73.8	24.10	23.20	1023	82.00	41.00
HoL$_3$·2H$_2$O	330-376	4.63	4.36	2	573-697	74.1	73.4	24.30	24.70	1001	94.20	47.10
ErL$_3$·2H$_2$O	340-423	4.62	4.10	2	587-697	73.9	73.7	24.50	24.70	1023	68.40	34.20
TmL$_3$·2H$_2$O	323-387	46.0	4.00	2	594-701	73.8	72.9	24.70	24.60	1033	60.90	30.45
YbL$_3$·2H$_2$O	323-416	4.69	4.63	2	565-658	73.4	72.9	25.70	26.00	990	58.50	29.25
LuL$_3$·2H$_2$O	323-373	4.57	4.40	2	573-705	73.2	73.0	25.30	26.00	973	74.20	37.10

For investigating if in low temperature the nature of atomic magnetic interactions is being changed the magnetic susceptibility of the Gd(III) complex was measured at 1.8–303 K. From the obtained results it appears that the complexes obey Curie-Weiss law.[5,7,32-37] The effective magnetic moment values experimentally determined in the temperature range of 77–303 K for 4-nitrocinnamates change from: 2.73 μ_B (at 76 K) to 3.22 μ_B (at 303 K) for Pr(III); 3.08 μ_B (at 76 K) to 3.55 μ_B (at 303 K) for Nd(III); 1.69 μ_B (at 76 K)

to 2.00 μ_B (at 303 K) for Sm(III); 1.81 μ_B (at 76 K) to 3.12 μ_B (at 303 K) for Eu(III); 7.81 μ_B (at 76 K) to 7.52 μ_B (at 303 K) for Gd(III); 9.06 μ_B (at 76 K) to 9.51 μ_B (at 303 K) for Tb(III); 10.88 μ_B (at 76 K) to 11.18 μ_B (at 303 K) for Dy(III); 9.97 μ_B (at 76 K) to 10.43 μ_B (at 303 K) for Ho(III); 9.25 μ_B (at 76 K) to 9.47μ_B (at 303 K) for Er(III); 7.12 μ_B (at 76 K) to 7.67 μ_B (at 303 K) for Tm(III) and 3.60 μ_B (at 76 K) to 4.39μ_B (at 303 K) for Yb(III).
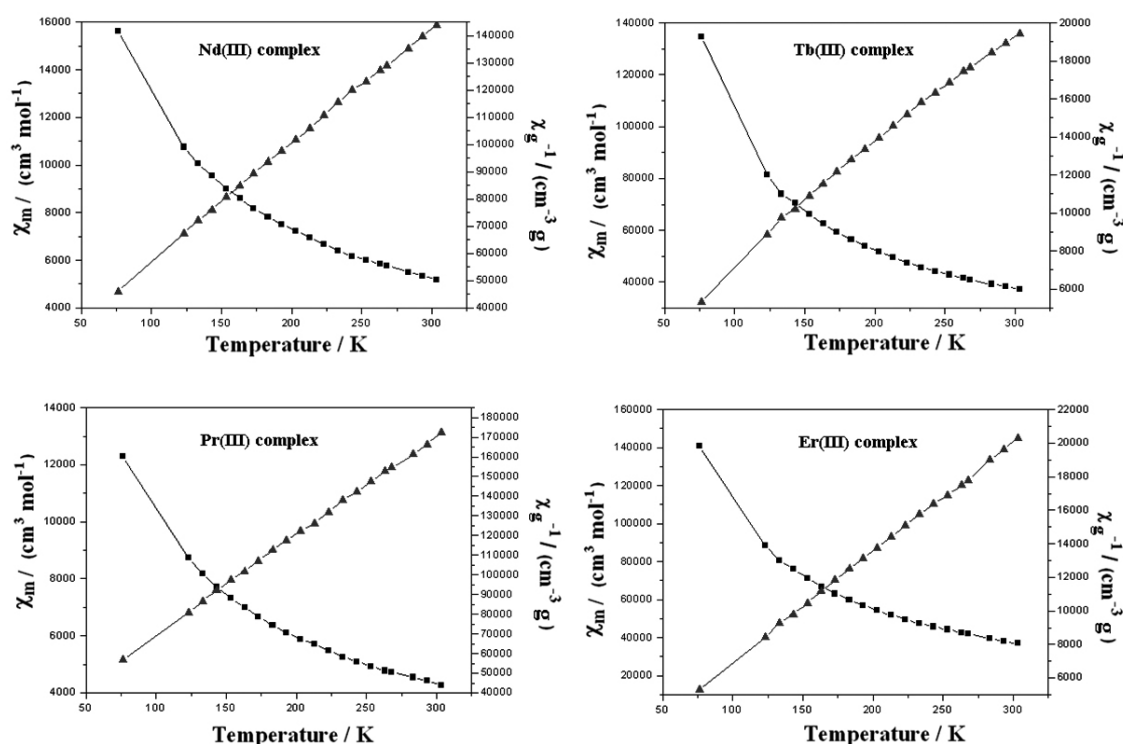
Fig. 4. Dependence of χ_m (black) values and χ_g^{-1} (blue) versus T for 4-nitrocinnamate of Nd(III), Pr(III), Tb(III) and Er(III).

In 4-nitrocinnamates of lanthanides(III) the paramagnetic central ions remain practically unaffected by diamagnetic ligands coordinated around them. The 4f orbitals, partly occupied by the magnetically active electrons are very efficiently shielded by the fully occupied 5s and 5p orbitals. These 4f orbitals are almost uninvolved in the bonds between a rare earth(III) ion and its nearest neighbors. The lanthanide(III) ion in a molecular compound behaves as free ion, and their energy levels are the same as in the free ions. The energy separation between the state of lowest energy and the first excited state varies from a few hundred to several thousands of wavenumbers. When this energy separation is weak the first excited state may be thermally populated while it is large, only the ground state is thermally populated. The ground electronic configuration together with ground and first excited states, and their energy separation are given in Table 4. The magnetic properties can be taken as those of the ground state alone, and lanthanide(III) ions in the compound act in the same way as free ions. The values of μ_{eff} determined for all 4-nitrocinnamates (except for europium) are close to those calculated for Ln(III) ions by Hund and van Vleck,[33] (Table 4).

Table 4. Magnetic moment values of lanthanide(III) ions calculated by Hund and Van Vleck[33] and those obtained experimentally at room temperature for 4-nitrocinnamates of Ln(III).

Trivalent ion	Configuration $4f^n$	μ_{eff}/μ_β calculated by Hund	μ_{eff}/μ_β calculated by Van Vleck	μ_{eff}/μ_β of complexes
Pr	$4f^2$	3.58	3.62	3.22
Nd	$4f^3$	3.62	3.68	3.54
Sm	$4f^5$	0.84	1.55-1.65	1.99
Eu	$4f^6$	0.00	3.40-3.51	3.09
Gd	$4f^7$	7.94	7.94	7.50
Tb	$4f^8$	9.70	9.70	9.46
Dy	$4f^9$	10.60	10.60	11.14
Ho	$4f^{10}$	10.60	10.60	10.41
Er	$4f^{11}$	9.60	9.60	9.47
Tm	$4f^{12}$	7.60	7.60	7.64
Yb	$4f^{13}$	4.50	4.50	4.38

The values of magnetic moments determined for all complexes indicate that the energies of 4f electrons in the central ions are not changed compared to those in the free lanthanide ions. Therefore the colours of complexes determined by rare earth element(III) ions stay the same as those in the free lanthanides. The electron density in the molecules makes the f-f electronic transitions of the central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths. The 4f orbitals of lanthanide(III) ions are effectively shielded by the $5s^25p^6$ octet. Therefore the metal-ligand bonding in analysed lanthanide(III) complexes is mainly electrostatic in nature.[34-36]

The magnetic properties of 4-nitrocinnamate of Gd(III) were studied over the temperature range of 1.8–300 K. Plots of magnetic susceptibility χ_m^{-1} and $\chi_m T$ product vs T (χ_m – molar magnetic susceptibility and T- temperature) are given in Figure 5.
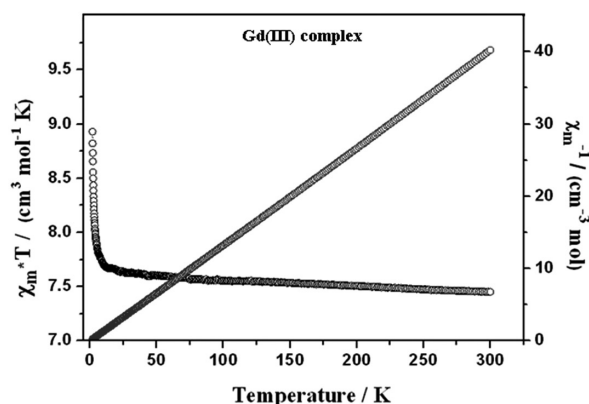

Fig. 5. Dependence of $\chi_m T$ (black) values and χ_m^{-1} (blue) versus T for 4-nitrocinnamate of Gd(III).

The temperature dependence of χ_m^{-1} obeys the Curie-Weiss law in the whole temperature range (as a result, a value $\theta = 0.37$ K was found). The small positive value obtained for θ implies a very weak ferromagnetic interaction in this Gd(III) complex in agreement with essentially constant $\chi_m T$ product as a function of temperature. At 300 K, $\chi_m T$ is equal to 7.45 cm^3mol^{-1}K which

roughly corresponds to the theoretical value calculated by Kahn[9] ($\chi_m T$ = 7.88 cm³Kmol⁻¹) for a free Gd^{III} ion (4f⁷, J = 7/2, L=0, S = 7/2, $^8S_{7/2}$ and g =2). The experimental curve $\chi_m T$ versus T shows the expected features for an isolated, mononuclear system of Gd^{III} ion. As temperature is lowering this curve exhibits a plateau from 300 to about 30 K, next increases steadily from 30 to 10 K and then more sharply down to 2 K. At temperature 2K $\chi_m T$ value is equal 8.92 cm³mol⁻¹K. The behavior observed below10 K is indicative of a weak ferromagnetic interaction between the Gd^{III} ions.[38, 39]

CONCLUSIONS

From the obtained results it follows that 4-nitrocinnamates of lanthanides(III) were prepared as mono- or dihydrates with colours typical for the particular Ln(III) ions. The Ln–O bonds are electrostatic in nature. The compounds are crystalline complexes that on heating in air to 1173 K decompose in two or three steps. In the first one all 4-nitrocinnamates dehydrate in one stage and form anhydrous compounds that next with rising temperature are directly decomposed (complexes of Pr(III) and Eu(III)) or with the intermediate formation of oxycarbonates (the rest of analysed complexes) to the oxides of the respective metals. The values of μ_{eff} calculated for all compounds are close to those obtained for Ln(III) ions by Hund and Van Vleck. There is no influence of the ligand field on the 4f electrons of lanthanide(III) ions.

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