

SPECTRAL, THERMAL AND MAGNETIC STUDIES OF 2-CHLORO-5-NITROBENZOATES OF RARE EARTH ELEMENTS(III)

W. Ferenc^{}, B. Bocian and A. Walków-Dziewulska*

Faculty of Chemistry, Maria Curie-Skłodowska University, Pl 20-031 Lublin, Poland

(Received October 16, 2003)

Abstract

The conditions of the formation of yttrium(III) and lanthanide(III) 2-chloro-5-nitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K were determined. The compounds are dihydrates and their solubilities are of the order of 10^{-3} mol dm⁻³. The FTIR, FIR and X-ray spectra for the complexes were recorded. All complexes are crystalline compounds. Their thermal decomposition was studied only in the range 293–523 K since on heating above 523 K the complexes decompose explosively. Hydrated 2-chloro-5-nitrobenzoates of rare earth elements lose two crystallization water molecules in one step. The enthalpy of dehydration process was established and the magnetic moments of the complexes were determined in the range 77–300 K. The compounds obey the Curie–Weiss law. The 4f electrons do not participate in the formation of the Ln–O bonds.

Keywords: 2-chloro-5-nitrobenzoates, complexes of rare earth elements, magnetic properties, spectroscopic investigations, thermal stability

Introduction

A survey of literature shows that the complexes of rare earth and *d*-block elements with such ligands as: 5-chloro-2-methoxy-, 4-chloro-2-nitro-, 4-chloro-3-nitro-, 2,3-, 2,4- and 3,4-dimethoxybenzoic acids have been obtained in solid-states and some of their physico-chemical properties including their thermal stability in air and nitrogen atmospheres have been studied [1–8]. Literature informs also about the complexes of 2-chloro-5-nitrobenzoates only with light lanthanides(III) as solids and about their properties [9]. In this work we present the synthesis of 2-chloro-5-nitrobenzoates with all rare earth elements(III) and their characterization by elemental analysis, FTIR and FIR spectral data, thermogravimetric studies and X-ray diffraction and magnetic measurements. The solubilities of these compounds were also determined in water at 293 K. The FTIR and FIR spectra were recorded in order to investigate the compositions of the complexes, to estimate the dentates of carboxylate groups and to

* Author for correspondence: E-mail: wetafer@hermes.umcs.lublin.pl

verify whether or not the lanthanide(III) 2-chloro-5-nitrobenzoates were converted to the nitrito isomers during precipitation or on heating to 573 K.

In order to estimate the crystalline structure of the complexes their X-ray powder diffraction measurements were recorded. The investigations of thermal stability of complexes let us know the mechanisms of dehydration and decomposition processes and estimate the position of crystallization water molecules in the complexes. In order to know the character of M–O bonding in the complexes and to answer why the colours of these complexes are typical for the appropriate trivalent lanthanide ions their magnetic susceptibilities were measured. The determination of solubilities of the complexes is valuable because it can give information about the practical use of 2-chloro-5-nitrobenzoic acid for separation of rare earth elements(III) by extraction or ion-exchange chromatographic methods.

The results of investigations presented in this work let us investigate the influence of substituent positions in benzene ring on the properties of the complexes of rare earth elements(III) with 5-chloro-2-methoxy-, 4-chloro-2-nitro-, 4-chloro-3-nitrobenzoic acids which will be the subject of our next paper.

Experimental

The 2-chloro-5-nitrobenzoates of lanthanides(III) were prepared by adding equivalent amounts of 0.1 M ammonium 2-chloro-5-nitrobenzoate at pH=5 to a hot solution containing the nitrate salts of the lanthanides(III), followed by crystallization at 293 K. The formed solids were filtered off, washed with hot water to remove ammonium ions and dried at 303 K.

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a Perkin Elmer CHN 2400 analyser. The contents of the Cl was determined by Schöniger method and the metal(III) ions and crystallization water spectrophotometrically and on the basis of TG curves, respectively (Table 1).

The FTIR and FIR spectra of complexes were recorded over the range 4000–400 and 600–100 cm^{-1} using FTIR 1725 Perkin Elmer and DIGILAB FTS-14 spectrometers, respectively. Samples for FTIR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Apiezon L suspension (Table 2, Fig. 1).

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\theta=4-80^\circ$ by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of the prepared complexes were investigated using Paulik–Erdey Q-1500D derivatograph with a Derill converter recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} . The 100 mg samples were heated in platinum crucibles in static air to 523 K. The DTG and DTA sensitivities were regulated by the Derill computer program and Al_2O_3 was used as the standard. The content of products of dehydration were calculated from the TG curves. Their chemical composition was verified by recording the diffraction pattern (Table 3, Fig. 2).

Table 1 Elemental analysis data of yttrium(III) and lanthanide(III) 2-chloro-5-nitrobenzoates

Complex	H/%		C/%		Cl/%		N/%		M/%	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$L=C_7H_3O_4NCl$										
LaL ₃ ·2H ₂ O	1.69	1.53	32.48	32.51	13.69	13.70	5.41	5.38	17.89	17.83
CeL ₃ ·2H ₂ O	1.68	1.54	32.43	32.53	13.67	13.68	5.40	5.35	18.01	17.96
PrL ₃ ·2H ₂ O	1.68	1.55	32.40	32.46	13.66	13.72	5.40	5.29	18.10	18.10
NdL ₃ ·2H ₂ O	1.66	1.60	32.24	32.30	13.63	13.60	5.37	5.29	18.45	18.42
SmL ₃ ·2H ₂ O	1.66	1.52	32.01	32.10	13.60	13.64	5.33	5.41	19.08	19.06
EuL ₃ ·2H ₂ O	1.66	1.59	31.94	31.96	13.50	13.58	5.32	5.30	19.24	19.29
GdL ₃ ·2H ₂ O	1.64	1.58	31.71	31.68	13.40	13.36	5.28	5.19	19.79	19.67
TbL ₃ ·2H ₂ O	1.63	1.55	31.65	31.62	13.38	13.34	5.28	5.20	19.95	19.86
DyL ₃ ·2H ₂ O	1.63	1.60	31.50	31.53	13.32	13.30	5.25	5.21	20.36	20.31
HoL ₃ ·2H ₂ O	1.62	1.62	30.72	31.02	13.26	13.20	5.16	5.15	20.55	20.49
ErL ₃ ·2H ₂ O	1.62	1.42	31.32	31.34	13.24	13.20	5.22	5.20	20.76	20.75
TmL ₃ ·2H ₂ O	1.76	1.72	34.21	34.20	14.46	13.42	5.70	5.68	22.93	22.80
YbL ₃ ·2H ₂ O	1.73	1.70	31.09	31.08	13.14	13.15	5.18	5.10	21.31	21.34
LuL ₃ ·2H ₂ O	1.60	1.58	31.01	31.00	13.10	13.06	5.16	5.12	21.53	21.48
YL ₃ ·2H ₂ O	1.79	1.70	34.69	34.85	13.14	13.15	5.78	5.30	12.24	12.23

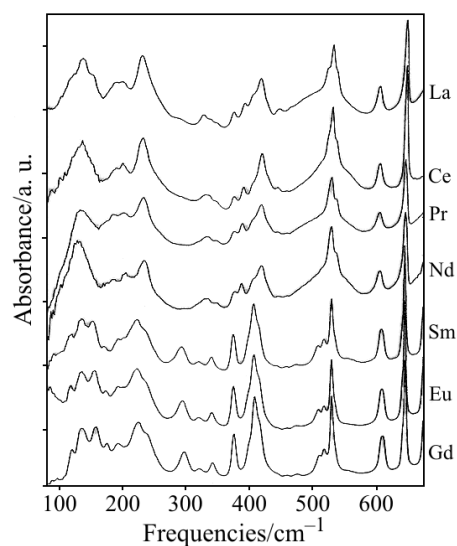


Fig. 1 Far-infrared spectra of 2-chloro-5-nitrobenzoates of light lanthanides(III)

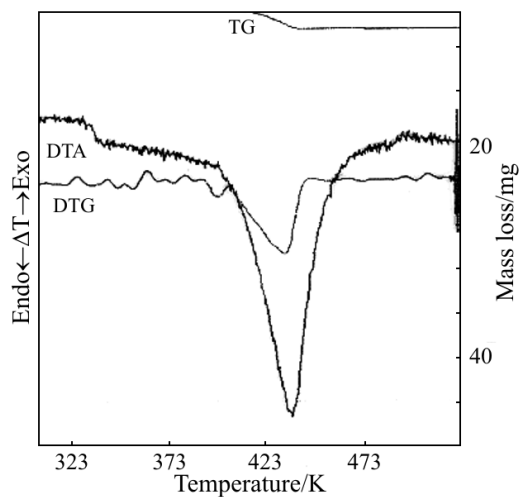


Fig. 2 TG, DTG and DTA curves of neodymium(III) 2-chloro-5-nitrobenzoate

The simultaneous TG-DSC analysis was carried out within 293–1150 K using a Netzsch STA 409C 3F differential thermoanalyser at a heating rate of 1 K min^{-1} . The experiments were carried out under argon flow at a rate of 75 mL min^{-1} (Fig. 3). The mass of samples ranged between 5.1 and 2.9 mg. The samples were heated in platinum crucibles without cover. On the basis of DSC curves the temperature of the beginning and heats of dehydration were determined.

Table 2 Wavenumbers (cm^{-1}) of COO^- band in 2-chloro-5-nitrobenzoates of yttrium(III), lanthanides(III) and sodium and of the COOH band in 2-chloro-5-nitrobenzoic acid

Complex $L=\text{C}_7\text{H}_3\text{O}_4\text{NCl}$	$\nu_{(\text{C}=\text{O})}$	ν_{asCOO^-}	ν_{sCOO^-}	$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{C-Cl}}$	$\nu_{\text{M-O}}$
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	–	1570	1395	175	750	435
$\text{CeL}_3 \cdot 2\text{H}_2\text{O}$	–	1565	1395	170	750	430
$\text{PrL}_3 \cdot 2\text{H}_2\text{O}$	–	1570	1395	175	750	430
$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$	–	1570	1395	175	750	430
$\text{SmL}_3 \cdot 2\text{H}_2\text{O}$	–	1570	1395	175	750	430
$\text{EuL}_3 \cdot 2\text{H}_2\text{O}$	–	1570	1395	175	750	425
$\text{GdL}_3 \cdot 2\text{H}_2\text{O}$	–	1590	1380	210	745	425
$\text{TbL}_3 \cdot 2\text{H}_2\text{O}$	–	1590	1385	205	745	420
$\text{DyL}_3 \cdot 2\text{H}_2\text{O}$	–	1595	1385	210	745	420
$\text{HoL}_3 \cdot 2\text{H}_2\text{O}$	–	1590	1380	210	747	425
$\text{ErL}_3 \cdot 2\text{H}_2\text{O}$	–	1595	1380	215	745	420
$\text{TmL}_3 \cdot 2\text{H}_2\text{O}$	–	1590	1380	210	745	420
$\text{YbL}_3 \cdot 2\text{H}_2\text{O}$	–	1600	1390	210	745	420
$\text{LuL}_3 \cdot 2\text{H}_2\text{O}$	–	1600	1380	220	745	425
$\text{YL}_3 \cdot 2\text{H}_2\text{O}$	–	1600	1380	220	750	425
HL	1707	–	–	–	740	–
NaL	–	1610	1380	230	744	–

The solubilities of 2-chloro-5-nitrobenzoates of rare earth elements(III) in saturated solutions were determined by a spectrophotometric method, using a spectrophotometer Specord M-40 (Table 3). The absorbance of the complexes was measured by using the Arsenazo III in the formic buffer (pH=3.5) and the wavelength $\lambda=650$ nm [10, 11].

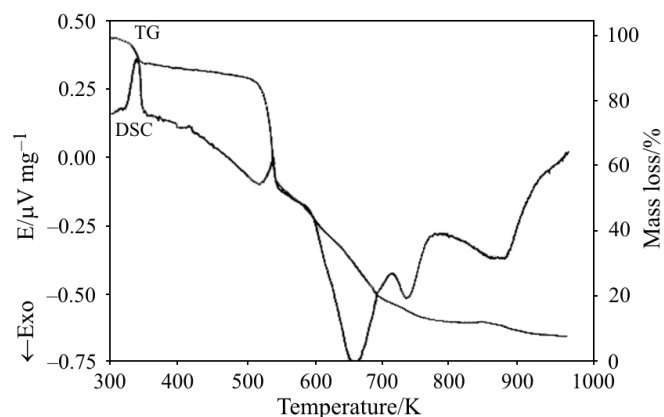
**Fig. 3** TG and DSC curves of 2-chloro-5-nitrobenzoate of terbium(III)

Table 3 Temperature range of dehydration of lanthanide(III) and yttrium(III) 2-chloro-5-nitrobenzoates in air atmosphere and their solubility in water at 293 K

Complex $L=C_7H_3O_4NCl$	$\Delta T/K$	T_{max}/K	Mass loss/%		n	$\Delta H/kJ mol^{-1}$	Solubility $10^{-3}/mol dm^{-3}$
			calculated	found			
LaL ₃ ·2H ₂ O	409–439	437	4.64	4.54	2	106.12	4.00
CeL ₃ ·2H ₂ O	402–439	432	4.63	4.53	2	106.04	2.90
PrL ₃ ·2H ₂ O	404–440	435	4.63	4.56	2	104.76	2.60
NdL ₃ ·2H ₂ O	408–443	440	4.60	4.55	2	106.24	2.20
SmL ₃ ·2H ₂ O	409–444	434	4.57	4.50	2	101.20	2.10
EuL ₃ ·2H ₂ O	399–445	438	4.56	4.50	2	109.85	2.00
GdL ₃ ·2H ₂ O	390–442	440	4.52	4.48	2	105.82	1.96
TbL ₃ ·2H ₂ O	344–380	360	4.52	4.50	2	104.19	1.62
DyL ₃ ·2H ₂ O	396–451	444	4.50	4.30	2	120.97	1.54
HoL ₃ ·2H ₂ O	394–442	436	4.49	4.36	2	102.03	1.46
ErL ₃ ·2H ₂ O	391–430	426	4.50	4.50	2	113.95	2.60
TmL ₃ ·2H ₂ O	390–428	422	4.80	4.72	2	107.29	2.40
YbL ₃ ·2H ₂ O	373–412	405	4.40	4.38	2	101.42	1.90
LuL ₃ ·2H ₂ O	378–417	406	4.43	4.40	2	125.06	1.50
YL ₃ ·2H ₂ O	385–431	425	5.00	5.30	2	121.40	3.10

ΔT – temperature range of dehydration process; T_{max} – temperature of the maximum of the endothermic effect in the DTA curve; n – number of crystallization water molecules being lost in one endothermic step; ΔH – enthalpy for dehydration process

Magnetic behaviour of the complexes at low temperatures and the magnetizations of the samples at 4.3 K were investigated at a magnetic field strength of 0–56 kOe (Figs 4–6). The measurements were carried out using ‘Lake Shore’ 7225 device (the DC magnetometer and the AC susceptometer). On the basis of the obtained results the magnetic susceptibility was determined according to Eq. (1):

$$\chi = \frac{M}{H} \quad (1)$$

where M is magnetisation, H is the applied magnetic field and its dependence between the values of the field strengths is presented in Fig. 5. The magnetic susceptibilities of the samples were studied only at the magnetic field strength of 0.5 kOe, in which there is the maximum of the susceptibility, and temperature 4.4–200 K. The parameters of the fitting

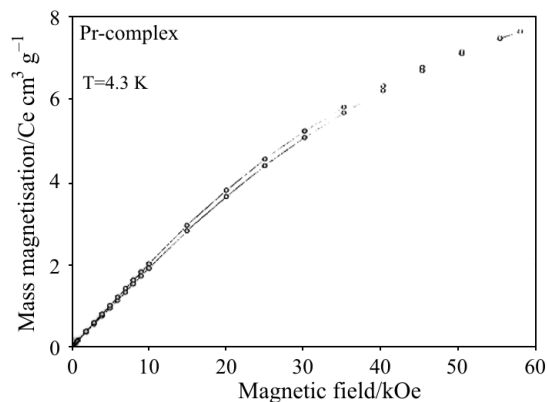


Fig. 4 Dependence between magnetization and magnetic field for 2-chloro-5-nitrobenzoate of praseodymium(III)

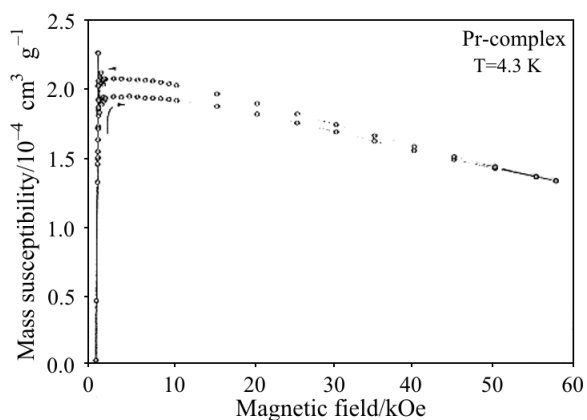


Fig. 5 Relationship between mass susceptibility and magnetic field for 2-chloro-5-nitrobenzoate of praseodymium(III)

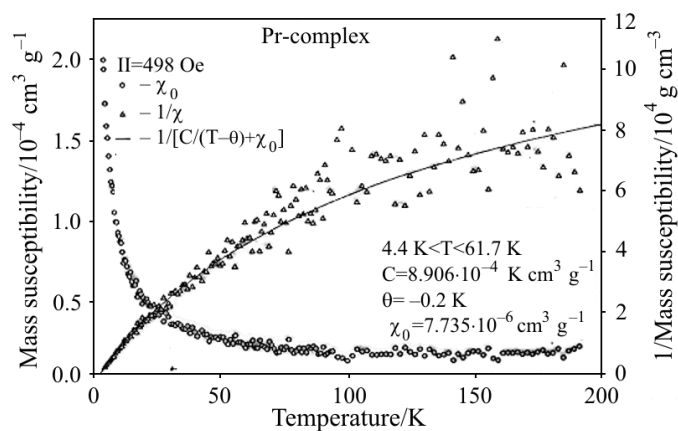


Fig. 6 Mass susceptibility for 2-chloro-5-nitrobenzoate of Pr(III) as a function of temperature to Curie–Weiss law are presented in Fig. 6. The alternating current susceptibilities in the narrow temperature range were measured using AC susceptometer.

Table 4 Values of μ_{eff} for the lanthanides determined by Hund and Van Vleck and calculated for lanthanide(III) 2-chloro-5-nitrobenzoates at 298 K

Ln^{3+}	Ground term	μ_{eff} determined by		$\mu_{\text{eff}}^{298\text{ K}}/\text{BM}$
		Hund	van Vleck	
La ³⁺	¹ S ₀	0.00	0.00	0.00
Ce ³⁺	² F _{5/2}	2.54	2.56	2.58
Pr ³⁺	³ H ₄	3.58	3.62	3.64
Nd ³⁺	⁴ H _{9/2}	3.62	3.68	3.72
Sm ³⁺	⁵ H _{5/2}	0.84	1.55–1.65	1.78
Eu ³⁺	⁷ H ₀	0.00	3.40–3.51	5.5
Gd ³⁺	⁸ S _{7/2}	7.94	7.94	7.84
Tb ³⁺	⁷ F ₆	9.70	9.70	9.68
Dy ³⁺	⁷ H _{15/2}	10.60	10.60	10.58
Ho ³⁺	⁵ J ₈	10.60	10.60	10.54
Er ³⁺	⁴ J _{15/2}	9.60	9.60	9.58
Tm ³⁺	³ H ₆	7.60	7.60	7.56
Yb ³⁺	² F _{7/2}	4.50	4.50	4.52
Lu ³⁺	¹ S ₀	0.00	0.00	0.00

Magnetic susceptibilities of polycrystalline samples of 2-chloro-5-nitrobenzoates were determined by Gouy method using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of 9.9 kOe. Co[Hg(SCN)₄] with the

magnetic susceptibility [12] of $1.644 \cdot 10^{-5} \text{ cm}^3 \text{ g}^{-1}$ was employed as calibrant. The correction for diamagnetism of the constituent atoms was calculated by using of Pascal's constants [13]. The magnetism of the samples was found to be field independent. The temperature-independent magnetism of the lanthanide ions was assumed to be zero. The magnetic moments were calculated according to Eqs (2) and (3):

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

$$\mu_{\text{eff}} = 2.83[\chi_M(T - \Theta)]^{1/2} \quad (3)$$

where Θ is the Weiss constant.

The magnetic moment values calculated for 2-chloro-5-nitrobenzoates of lanthanides(III) at 298 K, μ_{eff} , are presented in Table 4.

Results and discussion

2-Chloro-5-nitrobenzoates of rare earth elements(III) were obtained as crystalline substances with a metal to ligand ratio of 1:3 and a general formula $M(\text{C}_7\text{H}_3\text{NO}_4\text{Cl})_3 \cdot 2\text{H}_2\text{O}$, for $M = \text{La} - \text{Lu}$ and Y. The colours of the complexes are typical of the appropriate trivalent ions. In the molecules of 2-chloro-5-nitrobenzoates electrons of Cl atom and NO_2 groups are conjugated with Π electrons of aromatic ring. In these molecules the $f \rightarrow f$ electronic transitions of the central ions are of the lowest energy and absorption occurs at relatively high wavelengths depending on the nature of the metal ion [14–18].

The solid-state IR spectra of all complexes are quite similar but they are different from spectrum of the 2-chloro-5-nitrobenzoic acid. In the spectrum of acid the band at 1707 cm^{-1} , due to the presence of the COOH group is seen. This band is absent in the spectra of complexes where two bands arising from asymmetric and symmetric stretching vibrations of COO^- group occur at $1595 - 1565$ and $1395 - 1380 \text{ cm}^{-1}$, respectively. The bands with the maxima at $3700 - 3100 \text{ cm}^{-1}$ characteristic for $\nu(\text{OH})$ vibrations, narrow bands due to $\delta(\text{H}_2\text{O})$ at 1620 cm^{-1} and bending OH vibrations at 935 cm^{-1} confirm the presence of water in crystalline phase of complexes [19–29]. The infrared spectrum of 2-chloro-5-nitrobenzoic acid shows the bands at 1540 and 1360 cm^{-1} , which can be assigned to asymmetric and symmetric vibrations of the NO_2 group, respectively, the bands due to $\nu(\text{C}-\text{Cl})$ vibrations at $750 - 745 \text{ cm}^{-1}$ and the bands due to $\nu(\text{C}-\text{H})$ vibrations at $1160 - 1060$, $860 - 810$ and $670 - 550 \text{ cm}^{-1}$. The skeleton vibrations appear at 1610 , 1480 , 1430 and 1265 cm^{-1} . In the IR spectra of 2-chloro-5-nitrobenzoates of rare earth elements(III) the bands at 1540 and $1355 - 1350 \text{ cm}^{-1}$ are assigned to asymmetric and symmetric 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 coordinated to the metal ions. The $\nu(\text{C}-\text{Cl})$ vibrations occur at $750 - 740 \text{ cm}^{-1}$ and the bands at $435 - 420 \text{ cm}^{-1}$ are assigned to the metal-oxygen bond. These bands are not shifted to higher frequencies with increasing atomic number of lanthanide elements. This may suggest that complexes of 2-chloro-5-nitrobenzoic acid with lanthanides(III) exhibit similar stabilities [19, 22, 29]. The bands relevant to skeleton vibrations in IR spectra of complexes are shifted to lower frequencies compared to those in the acid spectrum. The

changes in their position are caused by the interaction between aromatic ring vibrations and the groups of atoms and ions. The bands in the range $130\text{--}125\text{ cm}^{-1}$ are connected with the O–H...O stretching vibrations and they change their shapes in the series of lanthanide(III) complexes. It probably results from the various size of lanthanide ions. The molecules of crystallization water probably remain in the outer coordination sphere and form hydrogen bonds [30, 31]. The bands at $155\text{--}140\text{ cm}^{-1}$ are due to C–C torsion vibrations. The bands at $249\text{--}240\text{ cm}^{-1}$ due to the aromatic ring vibrations are shifted to higher frequencies from La to Lu with the decrease of ionic radii of elements (Fig. 1). The bands of $\rho(\text{H}_2\text{O})$ vibrations appear at 530 cm^{-1} and they change their shapes in the series of lanthanides depending on the size of ionic lanthanides. The maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- for 2-chloro-5-nitrobenzoates of lanthanides(III), yttrium(III) and sodium are presented in Table 2. The magnitudes of separation, $\Delta\nu$, between the frequencies of ν_{asOCO} and ν_{sOCO} in the complexes are lower ($\Delta\nu=220\text{--}170\text{ cm}^{-1}$) than the sodium salt ($\Delta\nu=230\text{ cm}^{-1}$) which indicates a smaller degree of ionic bond in yttrium(III) and lanthanide(III) 2-chloro-5-nitrobenzoates. In the case of 2-chloro-5-nitrobenzoates of yttrium(III) and lanthanides(III) the shifts of the frequencies ν_{asOCO} and ν_{sOCO} are lower and higher, respectively, than those for sodium 2-chloro-5-nitrobenzoate. Therefore, the carboxylate ion appears to be a symmetrical, bidentate chelating ligand [19, 20, 32].

In order to verify whether or not the prepared lanthanide(III) 2-chloro-5-nitrobenzoates were converted to the nitrito isomers (during precipitation or on heating to 573 K) their FTIR spectra and FTIR spectrum of sodium nitrite were recorded. A survey of the literature shows that under influence of sunlight or with rising temperature the nitro complex may be transformed to the nitrito analogue in an endothermic process [33]. It was found that the isomerization of the nitro group may accompany the dehydration process of the complexes or be connected with the transformation process in its inner sphere [34]. As a monodentate ligand, nitrite ion may be bonded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrito compound. The general effect of coordination via nitrogen is an increase in the frequencies of the both ν_{asNO_2} and ν_{sNO_2} compared to the values characteristic for the free ion (~ 1328 and 1260 cm^{-1} , respectively [35]). The IR spectra recorded for all hydrated and dehydrated 2-chloro-5-nitrobenzoates of lanthanides(III) show that the nitro group is not transformed to the nitrito one with increase of temperature. No bands confirming isomerization of the nitro group through the oxygen atom were observed [34, 35].

In order to evaluate in which structure lanthanide(III) 2-chloro-5-nitrobenzoates crystallize, their X-ray powder diffraction measurements were carried out. The analysis of diffractogram suggests that they are polycrystalline compounds with low symmetry, large size of the unit cells and different structures. The complexes seem to be isostructural in two groups: La, Ce, Nd and Pr, Sm, Eu. Their structures have not been determined because single crystals of these compounds could not be obtained.

Preliminary investigations of the thermal stability of light lanthanide(III) 2-chloro-5-nitrobenzoates have shown that these complexes explosively decompose when heated in air above 573 K. Their instability above 573 K is most probably due to the presence of NO_2 group in benzene ring.

When heated at 293–523 K in air they dehydrate in one step and form anhydrous salts in the temperature range 380–451 K. Mass losses estimated for dehydration process from TG curves are equal to 5.30–4.30% (the theoretical: 5.00–4.43%). The dehydration process is connected with an endothermic effect shown in the DTA curves [36, 37]. The derivatogram of neodymium(III) 2-chloro-5-nitrobenzoate is presented in Fig. 2. The mass loss of the complex starts at 408 K. The decrease in mass occurs in the range 408–443 K and therefore the TG curve deviates from horizontal. The loss in mass determined from TG curve is equal to 4.55% (the calculated value is 4.60%) which corresponds to the lost of two molecules of water crystallization [36, 37]. The peak ascribed to this loss of mass is also recorded in the DTG curve. The anhydrous 2-chloro-5-nitrobenzoates of rare earth elements(III) decomposed during heating in air to 1173 K to the oxides of the respective metals, which were identified by X-ray powder diffraction [38, 39]. From the results obtained it follows that the molecules of water bind in the outer coordination sphere of the complexes [40–42]. Crystallization water is removed from various compounds in a broad temperature range [36, 37, 40–42]. According to Nikolaev *et al.* [40–42] and Singh *et al.* [43], water eliminated below 413–423 K can be considered as crystallization water and water eliminated above 423 K – as one coordinated to the central ion. In our case water is eliminated below 413 K and IR studies seem to indicate that we are dealing with the crystallization water. The exact assignment of the position of water molecules would be possible on the basis of X-ray data which were unable to obtain on the lack of suitable single crystals.

The thermogravimetric studies of 2-chloro-5-nitrobenzoates of lanthanides(III) and yttrium(III) were carried out with simultaneous TG-DSC analysis in the temperature range 293–973 K (Table 3, Fig. 3). The obtained results reveal the complexes to be dihydrates. They are stable up to 344–409 K. Next in the range 344–451 K they dehydrate in one step. The mass loss estimated from TG curves (4.36–5.30%) corresponds to the release loss of two molecules of water (the theoretical values are equal to 4.40–5.00%). The energetic effects ($\Delta H=101.20$ – 125.06 kJ mol⁻¹) accompanying this process confirm the losses of two molecules of water. The products of dehydration were characterized by elemental analysis, IR spectroscopy and X-ray powder analysis.

The solubility values of 2-chloro-5-nitrobenzoates of the lanthanides(III) in water (at 293 K) are summarized in Table 3. They are in order of 10⁻³ mol dm⁻³. Holmium(III) 2-chloro-5-nitrobenzoate is the least soluble complex, while the most soluble one is the complex of lanthanum(III). The values of solubility are not regularly changed in the series of complexes investigated. Low values of solubilities of 2-chloro-5-nitrobenzoic acid complexes indicate that 2-chloro-5-nitrobenzoic acid is not suitable for the separation of the lanthanide elements by ion-exchange chromatography or by extraction methods.

The magnetic susceptibility of lanthanide(III) 2-chloro-5-nitrobenzoates was determined in 4.4–300 K. All complexes show paramagnetic properties and they obey the Curie–Weiss law. The clear magnetic arrangement regions were not observed in the whole temperature range. As an example, the parameters of the fitting to Curie–Weiss law for praseodymium(III) 2-chloro-5-nitrobenzoate are presented in Figs 4–6. The values of μ_{eff}

determined for all the complexes (except that for europium) are close to those calculated for Ln(III) ions by Hund and Van Vleck (Table 4). Paramagnetic behaviour of lanthanide (3+) ions is due to the presence of unpaired 4f electrons. Since these electrons are well shielded from external influence, both their spin and orbital motions are significant in determining the overall observed magnetic moment of a complex compound. It follows, therefore, that the magnetic moment of a complex should indicate whether or not these 4f electrons are involved in bond formation. The complexes discussed herein show little deviation from the Van Vleck values although the simple Curie equation has been used. It could be expected that the crystal field splitting of f-orbitals is of the order of 100 cm^{-1} , a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate levels have been split by the crystal field [44–46]. The values of magnetic moments (Table 4) indicate that La(III) and Lu(III) complexes are diamagnetic, as may be expected from their closed shell electronic configurations and the absence of unpaired electrons [47–49]. The higher value of μ_{eff} for europium(III) 2-chloro-5-nitrobenzoates compared with that given by Hund may suggest a possible interaction of the ligand field with central ion or may be associated with the multiplet splitting. The lowest three excited states of the europium ion are sufficiently close in energy to the ground state to be appreciably populated at room temperature [46, 50, 51]. Since the excited states possess higher J values than the ground state, the actual magnetic moment is larger than that calculated by using the J value for the ground state. With the exception of Sm and Eu, the multiplet widths for the lanthanide elements are very large compared with kT ($kT=200 \text{ cm}^{-1}$) at room temperature, whereas those for Sm and Eu are not really infinitely large compared to kT . For Eu the interval between the lowest multiplet components is only 1/21 of the overall width as for a ${}^7\text{F}$ term [46] it applies (Eq. (4)):

$$0.5[J_{\text{max}}(J_{\text{max}}+1)-J_{\text{min}}(J_{\text{min}}+J)]=0.5 \times 6 \times 7 - 0 = 21$$

$$J_{\text{min}}+1=1 \quad (4)$$

In the complexes of 2-chloro-5-nitrobenzoates the paramagnetic central ions remain virtually unaffected by the surrounding diamagnetic ligands. The 4f electrons causing their paramagnetism are well protected from outside influences and do not participate in the formation of the Ln–O bond. Instead, they only weakly interact with the electrons of the surrounding atoms [52]. Their energy levels are the same as in the free ions due to the very effective shielding by the overlapping $5s^25p^6$ shell. For the lanthanide ions the ground state is separated by several hundreds of cm^{-1} from the next higher-lying state. Hence, the magnetic properties can be considered identical to those of the ground state alone, making bonded lanthanide ions act in the same way as the free ions.

Concluding, from the obtained results it appears that the Ln–O bond in lanthanide(III) 2-chloro-5-nitrobenzoates is mainly electrostatic in nature, since the 4f orbitals of the lanthanide(III) ions are effectively shielded by the $5s^25p^6$ octet.

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