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Preparation and Properties of Yttrium, Lanthanum and Lanthanide *p*-Nitrobenzoates

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The conditions of the formation of rare earth element *p*-nitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K were determined (their solubilities are of the order of 10^{-3} mol dm^{-3}). The IR and X-ray spectra for the prepared complexes and the dehydrated rare earth *p*-nitrobenzoates were recorded. All obtained complexes are crystalline compounds. The conditions of thermal decomposition of the complexes were also studied. It was found that on heating above 573 K the complexes decompose explosively and undergo a melting process at the same time. Therefore the thermal decomposition for complexes being investigated was carried out in the temperature range 273–573 K. From the obtained results it follows that during the dehydration process no transformation of the nitro group to nitrito occurs.

(Keywords: Complexes; Lanthanoids)

Herstellung und Eigenschaften von Y, La *und Lanthaniden-p-nitrobenzoaten*

Die Bedingungen zur Darstellung von Y-, La- und Lanthaniden-*p*-nitrobenzoaten wurden untersucht. Ihre quantitative Zusammensetzung und ihre Wasserlöslichkeit bei 298 K wurden bestimmt (die Löslichkeit ist in der Größenordnung 10^{-3} mol dm^{-3}). Die Infrarot- und Röntgenspektren der erhaltenen Komplexe sowie der *p*-Nitrobenzoate der seltenen Erden nach der Dehydratisierung wurden gemessen und dabei festgestellt, daß es sich um kristalline Verbindungen handelt. Das thermische Verhalten der erhaltenen Komplexe wurde untersucht: Sie zerfallen über 573 K explosiv und schmelzen zugleich. Der thermische Zerfall der erhaltenen *p*-Nitrobenzoate der seltenen Erden wurde im Temperaturbereich von 273—573 K untersucht. Es wurde festgestellt, daß die Y-, La- und Lanthaniden-*p*-nitrobenzoate bei Temperaturzunahme oder im Dehydratisierungsprozeß keiner Umgruppierung in entsprechende Nitritoverbindungen unterliegen.

p-Nitrobenzoic acid is a yellow, crystalline solid, readily soluble in HNO_2 and sparingly soluble in water [1]. It crystallizes in a monoclinic system [2–6] and occurs in dimer form. The carboxylation process for *p*-nitrobenzoic acid [7–9] and the mechanism of its dissociation in various solvents [10] were studied and the heat of its combustion determined [11].

The salts of *p*-nitrobenzoic acid with the following cations have been isolated in the solid state and their properties studied: NH_4^+, Ag^+, Mg^{2+} [1], Na^+ [1, 12–14], K^+ [1, 15], Li^+ [16], Hg^{2+} [17], Ba^{2+} [18, 19], Cu^{2+} [1, 20–26], Ni^{2+} [27], Bi^{3+} [28], Pb^{4+} [29], Ti^{4+} [30], Zr^{4+} and Hf^{4+} [31], W^{6+} [32], Sc^{3+} [33], Th^{4+} [34], Nd^{3+} and Pr^{3+} [35–38], Dy^{3+} [39] and Eu^{3+} [40].

p-Nitrobenzoates of Pr(III), Nd(III), Eu(III) and Dy(III) were isolated in the solid state [35–40], their optical properties were investigated and the absorption spectra in the range 800–200 cm^{-1} were recorded [35].

The crystalline structure determined for *p*-nitrobenzoate of Dy(III) [39] appears to consist of tetrameric units $Dy_4(O_2CC_6H_4NO_2)_{12} \cdot 10\,H_2O$, in which four atoms of Dy are connected in a chain by the double bridge of the carboxylic ligands. Dysprosium *p*-nitrobenzoate crystallizes in the triclinic system. *p*-Nitrobenzoates of rare earth elements obtained by *Khiyalov* and *Musaev* were found to form dihydrates (for the light lanthanides) and trihydrates (for the heavy ones) [41].

The aim of this work was to obtain in solid state the *p*-nitrobenzoates of yttrium, lanthanum and lanthanides from Ce(III) to Lu, to examine some of their physico-chemical properties and to study the thermal decomposition.

Experimental

p-Nitrobenzoates of yttrium, lanthanum and lanthanides from Ce(III) to Lu were prepared by double decomposition, adding the equivalent quantities of 0.2 *M* ammonium *p*-nitrobenzoate (*pH* ~ 5) to a hot solution containing the rare earth element nitrates and crystallizing at 293 K. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant mass.

Carbon, hydrogen and nitrogen microanalysis data for these complexes were determined by elemental analysis with V_2O_5 as oxidizing agent. The rare earth element contents were established by the oxalic acid method.

The content of crystallization water molecules was determined from the TG curve and by isothermal heating of these complexes at 573 K. From the obtained results (Table 1) it appears that *p*-nitrobenzoates of rare earth elements are hydrated salts with a metal to ligand ratio of 1 : 3.

In order to confirm the chemical composition of the obtained salts, IR spectra for the prepared complexes, the spectra for *p*-nitrobenzoic acid, sodium *p*-nitrobenzoate, the dehydrated *p*-nitrobenzoate of yttrium, lanthanum and lanthanides and for sodium nitrite were recorded as KBr discs on a UR-20 spectrophotometer (range 4000–400 cm^{-1}). The experimental data are presented in Tables 2–4.

In order to study the crystal structure of *p*-nitrobenzoates of rare earth elements and the structure of the dehydrated complexes, the X-ray diffraction patterns were taken on a DRON-2 diffractometer using Ni filtered CuKα

Table 1. *Analytical data*

Compound $L = C_7H_4NO_4$	% C		% N		% H		% M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$YL_3 \cdot 3\,H_2O$	39.31	38.76	6.55	6.49	2.80	2.88	13.87	13.65
$LaL_3 \cdot 3\,H_2O$	36.47	35.98	6.07	6.33	2.60	2.41	20.10	19.88
$CeL_3 \cdot 3\,H_2O$	36.40	36.09	6.06	6.19	2.60	2.86	20.23	19.92
$PrL_3 \cdot 3\,H_2O$	36.36	36.50	6.06	6.01	2.59	2.43	20.33	20.41
$NdL_3 \cdot 3\,H_2O$	36.19	36.18	6.03	6.05	2.58	2.44	20.71	20.64
$SmL_3 \cdot 3\,H_2O$	34.98	34.22	5.83	5.64	2.49	2.24	20.87	20.67
$EuL_3 \cdot 3\,H_2O$	35.79	35.86	5.96	6.08	2.55	2.41	21.58	21.26
$GdL_3 \cdot 3\,H_2O$	35.53	35.58	5.92	5.81	2.53	2.63	22.17	22.12
$TbL_3 \cdot 3\,H_2O$	35.44	35.41	5.90	6.05	2.53	2.47	22.35	22.34
$DyL_3 \cdot 3\,H_2O$	35.26	35.86	5.87	5.87	2.51	2.39	22.74	22.68
$HoL_3 \cdot 3\,H_2O$	35.14	35.15	5.85	5.98	2.51	2.49	23.00	22.94
$ErL_3 \cdot 3\,H_2O$	35.03	35.09	5.83	5.91	2.50	2.62	23.25	23.31
$TmL_3 \cdot 3\,H_2O$	34.93	34.98	5.82	5.56	2.49	2.22	23.47	23.40
$YbL_3 \cdot 3\,H_2O$	34.75	34.24	5.79	5.84	2.48	2.38	23.86	23.68
$LuL_3 \cdot 3\,H_2O$	34.66	34.23	5.77	5.88	2.47	2.31	24.06	24.02

Table 2. *Frequencies of the maxima of absorption bands in the IR spectra of* Y, La, Gd, *and light lanthanide* p-*nitrobenzoates* *(cm^{-1})*

Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Assignments
3 460	3 460	3 480	3 500	3 460	3 530	3 450	3 450	stretching vibration of OH of HOH
1 630	1 620	1 625	1 625	1 620	1 620	1 625	1 625	asymmetrical vibration of COO^-
1 565	1 560	1 565	1 560	1 560	1 565	1 560	1 570	asymmetrical vibration of NO_2
1 430	1 425	1 425	1 420	1 420	1 425	1 425	1 430	symmetrical vibration of COO^-
1 355	1 350	1 355	1 355	1 350	1 350	1 355	1 355	symmetrical vibration of NO_2
1 110	1 110	1 110	1 110	1 110	1 110	1 110	1 110	stretching vibration of C—N
1 020	1 020	1 020	1 020	1 020	1 020	1 020	1 020	vibration of the neighbouring hydrogen atoms in the benzene ring
885	885	890	885	885	880	885	880	stretching vibration of C—H
850	845	845	845	845	845	845	845	stretching vibration of C—N
800	800	800	800	800	800	800	800	deformation vibration of NO_2
730	730	730	730	730	730	730	730	hydrogen atom vibrations in benzene ring
525	520	520	520	520	525	520	525	stretching vibration of the metal—oxygen bond

Table 3. *Frequencies of maxima of the absorption bands in the IR spectra of heavy lanthanides* p-*nitrobenzoates* (cm^{-1})

Tb	Dy	Ho	Er	Tm	Yb	Lu	Assignments
3 450	3 450	3 450	3 450	3 450	3 450	3 450	stretching vibration of OH of HOH
1 610	1 610	1 615	1 615	1 615	1 615	1 615	asymmetrical vibration of COO^-
1 560	1 550	1 560	1 560	1 560	1 570	1 560	asymmetrical vibration of NO_2
1 420	1 420	1 420	1 420	1 425	1 425	1 425	symmetrical vibration of COO^-
1 350	1 345	1 345	1 345	1 345	1 340	1 345	symmetrical vibration of NO_2
1 110	1 110	1 110	1 110	1 110	1 105	1 105	stretching vibration of C—N
1 020	1 020	1 020	1 020	1 020	1 015	1 015	vibration of the neighbouring hydrogen atoms in the benzene ring
880	880	880	885	880	880	880	stretching vibration of C—H
840	845	845	845	845	840	840	stretching vibration of C—N
800	800	800	800	800	800	800	deformation vibration of NO_2
730	730	730	730	730	725	730	hydrogen atom vibrations in benzene ring
520	520	525	525	520	525	525	stretching vibration of the metal—oxygen bond

Table 4. *Frequencies of maxima of the absorption bands of* COO^- *vibrations for* p-*nitrobenzoates of yttrium, lanthanum and lanthanides and for sodium* p-*nitrobenzoates*

Complex $L = C_7H_4NO_4$	$\bar{\nu}_{asym}$ OCO cm^{-1}	$\bar{\nu}_{sym}$ OCO cm^{-1}	$\Delta\bar{\nu}$
$YL_3 \cdot 3H_2O$	1 630	1 430	200
$LaL_3 \cdot 3H_2O$	1 620	1 420	200
$CeL_3 \cdot 3H_2O$	1 625	1 425	200
$PrL_3 \cdot 3H_2O$	1 625	1 425	200
$NdL_3 \cdot 3H_2O$	1 620	1 420	200
$SmL_3 \cdot 3H_2O$	1 620	1 420	200
$EuL_3 \cdot 3H_2O$	1 625	1 425	200
$GdL_3 \cdot 3H_2O$	1 625	1 430	195
$TbL_3 \cdot 3H_2O$	1 610	1 420	190
$DyL_3 \cdot 3H_2O$	1 610	1 420	190
$HoL_3 \cdot 3H_2O$	1 615	1 420	195
$ErL_3 \cdot 3H_2O$	1 615	1 420	195
$TmL_3 \cdot 3H_2O$	1 615	1 425	190
$YbL_3 \cdot 3H_2O$	1 615	1 425	190
$LuL_3 \cdot 3H_2O$	1 615	1 425	190
NaL	1 630	1 410	220

radiation. The measurements were made within the range $2\sigma = 4$–$80°$ by means of the *Debye-Scherrer* method.

The thermal stability of the complexes was studied by the use of TG, DTA and DTG technique. The measurements were made with a Q-1500 D derivatograph at a heating rate of 2.5 deg min^{-1}. Test samples were heated at a sensitivity TG—50 mg, DTG—500 μV, DTA—500 μV. In Table 5 the temperature ranges of the dehydration process for *p*-nitrogenzoates of yttrium, lanthanum and lanthanides are presented.

The solubilities of *p*-nitrobenzoates of Y, La and lanthanides in water at 298 K were determined by measuring the concentration of Ln^{3+} ions in saturated solutions by the oxalic acid method. The solubility values are given in Table 6.

Results and Discussion

p-Nitrobenzoates of rare earth elements were obtained in crystalline form with the colour characteristic for Ln^{3+} ions. In comparison with *p*-nitrobenzoates, all *o*-nitrobenzoates of Y, La and lanthanides form yellow solids [42].

The complexes of *p*-nitrobenzoates of rare earth elements were found to be trihydrates with the general formula: $Ln(C_7H_4NO_4)_3 \cdot 3H_2O$, where: *Ln* = Y, La, Ce—Lu.

p-Nitrobenzoates of Y, La and lanthanides prepared by *Khiyalov* and *Musaev* form two isostructural groups: dihydrates of *p*-nitrobenzoates of light lanthanides and trihydrates of heavy lanthanons and Y [41].

In the case of *p*-nitrobenzoates of rare earth elements no regular changes of the hydration degree with the ionic radius in the lanthanide series are observed.

p-Nitrobenzoic acid has sharp absorption bands of the OH group at ca. 3 600–2 700 cm^{-1}, a strong band of COOH at 1 710 cm^{-1}, the bands of asymmetric and symmetric vibrations of the NO_2 group at 1 555 cm^{-1} and 1 355 cm^{-1}, respectively, a band of the stretching vibration of the C—O group at 1 435 cm^{-1} and the band of valence vibration of C—N at 1 115 cm^{-1}.

The band of the ring vibrations for *para*-disubstituted compounds appears at ca. 1 020 cm^{-1}. The band at 940 cm^{-1} confirms the out-of-plane deformation vibration of the O—H group. The band of the C—H group vibration of the aromatic ring is observed at around 880 cm^{-1}. The band arising from the deformation vibration of the NO_2 group appears at 805 cm^{-1} and the bands at 565 cm^{-1} arise from the out-of-plane deformation vibration of C—H group.

The IR spectra for all the complexes are quite similar and their analysis confirms the formulations of *p*-nitrobenzoates obtained as nitro complexes.

The water leads to the characteristic absorptions in the 3 600–3 100 cm^{-1} range. When the acid is converted to the salt a change in the spectra is observed.

All the spectra of *p*-nitrobenzoates of rare earth elements show no bands at 1 710 cm^{-1} characteristic for COOH, which is indicative of the absence of the free COOH groups in the complexes. The bands arising from asymmetric and symmetric vibrations of the COO^- group appear at 1 610–1 630 cm^{-1} and 1 430–1 420 cm^{-1}, respectively. The bands occuring at 1 570–1 550 cm^{-1} and 1 355–1 340 cm^{-1} are assigned to asymmetric and symmetric vibration of NO_2 group, respectively. The bands at 800 cm^{-1} are indicative of the deformation vibration of NO_2 group.

The bands indicating the presence of the C—N group are observed at 1 110 cm^{-1} and the bands confirming the neighbouring hydrogen atom vibrations in the benzene ring substituted in 1 : 4 position occur at 1 020 cm^{-1} and 730 cm^{-1}, respectively. The absorption bands at 525–520 cm^{-1} confirm the ionic bond of metal—oxygen.

For all *p*-nitrobenzoates of yttrium, lanthanum and lanthanides no shift changes of these bands are observed. Accordingly, it is possible to suggest that *p*-nitrobenzoic acid forms with rare earth elements complexes of similar stabilities. In this case the comparison of the stabilities of *p*-nitrobenzoates seems to be possible since these complexes are of the same type.

In these complexes the vibrations of *M*-O are not the pure ones on account of the conjugation of C—O and C—C group vibrations. Table 4 shows the maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of $—COO^-$ for *p*-nitrobenzoates of rare earth elements and sodium.

The magnitudes of separation $\Delta\bar{\nu}$ between the frequencies due to $\bar{\nu}_{asym}$ OCO and $\bar{\nu}_{sym}$ OCO in the complexes are lower than in the sodium salt, which indicates a smaller degree of ionic bond in these complexes compared to that of sodium. Having a greater ionic potential than a sodium ion, lanthanide ions influence the ligand more strongly causing its greater deformation. From the analysis of the values for $\Delta\bar{\nu}$ presented in Table 4 it is not possible to define the degree of the covalent bond because of the changes of the OCO bond angle with the changes of ionic radii in the lanthanide ions. *p*-Nitrobenzoates of light lanthanides appear to have a larger $\Delta\bar{\nu}$ compared to *p*-nitrobenzoates of the heavy ones, which indicates the comparatively greater value of the ionic bond in *p*-nitrobenzoates of light lanthanides and lanthanum than in the case of the heavy ones. A similar relationship is observed for the complexes of *o*-nitrobenzoic acid with rare earth elements [42] but the values $\Delta\bar{\nu}$ are smaller relative to those of *p*-nitrobenzoates. It may be indicative for the influence of the NO_2 group position on the structure of complexes and on the mechanism of the reaction of their formation.

In the *para* position of the NO_2 group the inductive effect is stronger than in its *ortho* position. The conjugation of NO_2 with the benzene ring is comparatively weak.

In the systems containing the NO_2 group in *para* position the weak positive resonance effect occurs in the reaction centre [43]. In the IR spectra of *p*-nitrobenzoates of yttrium, lanthanum and lanthanides the relatively lower intensities of the bands at 880 cm^{-1} compared to that of *p*-nitrobenzoic acid indicate the weak interaction of the benzene ring with lanthanide ions in the obtained complexes.

The displacements in the positions of $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ bands for *p*-nitrobenzoates of rare earth elements relative to those in *p*-nitrobenzoic acid are indicative of the coordination of the NO_2 group to lanthanide ions. In IR spectra of *p*-nitrobenzoates of Y, La and lanthanides the directions of shifts in the frequencies due to ν_{asym} OCO and ν_{sym} OCO are lower (or unaltered) and higher, respectively, relative to those for sodium *p*-nitrobenzoate. According to this fact it is possible to assume that the carboxylate ion is a bidentate, chelating ligand.

From preliminary studies on the thermal stability of *p*-nitrobenzoates of rare earth elements it follows that on heating above 573 K the complexes are explosively decomposed at the melting point. A survey of literature shows that under the influence of sunlight or with the increase of temperature the transformation process of nitro complexes to nitrito ones (being connected with an endothermic effect) may proceed [44]. It was also found that the isomerisation of nitro groups may accompany the dehydration process of the complex or be connected with the transformation process in its inner sphere [45]. As monodentate ligand the nitrite ion may bond either through a nitrogen atom forming the nitro complex, or through one of the oxygen atoms yielding a nitrito complex. The general effect of coordination via nitrogen is to raise the frequencies of both $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ from the free ion values of ~ 1 328 cm^{-1} and ~ 1 260 cm^{-1}, respectively [46].

In order to verify if the obtained rare earth element *p*-nitrobenzoates do not convert to nitrito isomers (during precipitation or on heating to 573 K) the IR spectra for hydrates of *p*-nitrobenzoates of Y, La and lanthanides, for the dehydrated complexes of rare earth element *p*-nitrobenzoates and for sodium nitrite were recorded.

The results obtained show that the *p*-nitrobenzoates of rare earth elements isolated as solid form nitro complexes causing in the IR spectra of the complexes the frequencies of absorption bands due to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ at 1 595–1 580 cm^{-1} and 1 360–1 345 cm^{-1} respectively, are displaced to higher frequencies relative to those for the free NO_2^- ion.

The IR spectra recorded for all hydrated and dehydrated *p*-nitrobenzoates of rare earth elements reveal that no transformation process of the nitro group to nitrito takes place with rising temperature. In the IR spectra for all dehydrated *p*-nitrobenzoates of Y, La and lanthanides the absorption bands at 3 600–2 800 cm^{-1} disappear, which indicates that no crystallization water molecules are present in the dehydrated complexes. The remaining bands in the IR spectra for the dehydrated complexes remain unchanged with regard to those characteristic bands occuring in the hydrated complexes and are assigned to the same groups as it was presented for *p*-nitrobenzoates of rare earth elements.

On heating, *p*-nitrobenzoates of coloured lanthanide ions change their colours characteristic for Ln^{3+} ions and form white anhydrous complexes.

In order to examine the crystal structure of hydrated and dehydrated *p*-nitrobenzoates of rare earth elements and oxides (obtained from ignition of *p*-nitrobenzoates of Y, La and lanthanides) the X-ray spectra were recorded.

p-Nitrobenzoates were found to be crystalline compounds characterized by low symmetry, the large sizes of the unit cells and different structures (Figs. 1 and 2). Different from *o*-nitrobenzoates [42] or di- and trihydrates of rare earth elements prepared by *Khiyalov* and *Musaev* [41] the obtained salts are not isostructural. In the case of *o*-nitrobenzoates of Y, La and lanthanides only complexes of Tb, Dy and Ho are isostructural. *p*-Nitrobenzoates of rare earth elements obtained by *Khiyalov* and *Musaev* form the two isostructural groups with formulae $M(OOCC_6H_4NO_2)_3 \cdot 2\,H_2O$ from La to Gd and $M(OOC_6H_4NO_2)_3 \cdot 3\,H_2O$ from Tb to Lu, Y [41].

The slow heating of *p*-nitrobenzoates of Y, La and lanthanides in air leads to the formation of the oxides of appropriate lanthanons whose external forms are different from the rare earth element oxides obtained by the ignition of oxalates. Therefore X-ray spectra for yttrium, lanth-

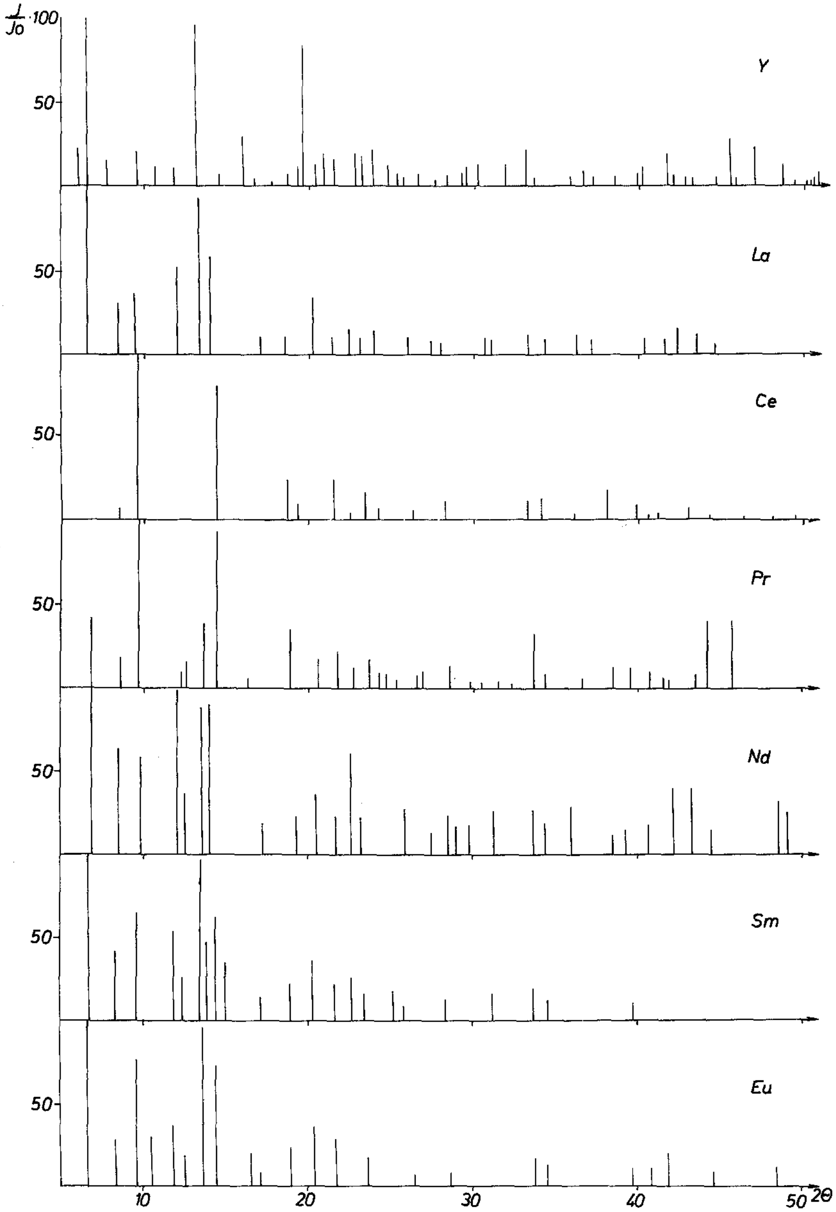

Fig. 1. Radiograms of *p*-nitrobenzoates of Y, La and light lanthanides

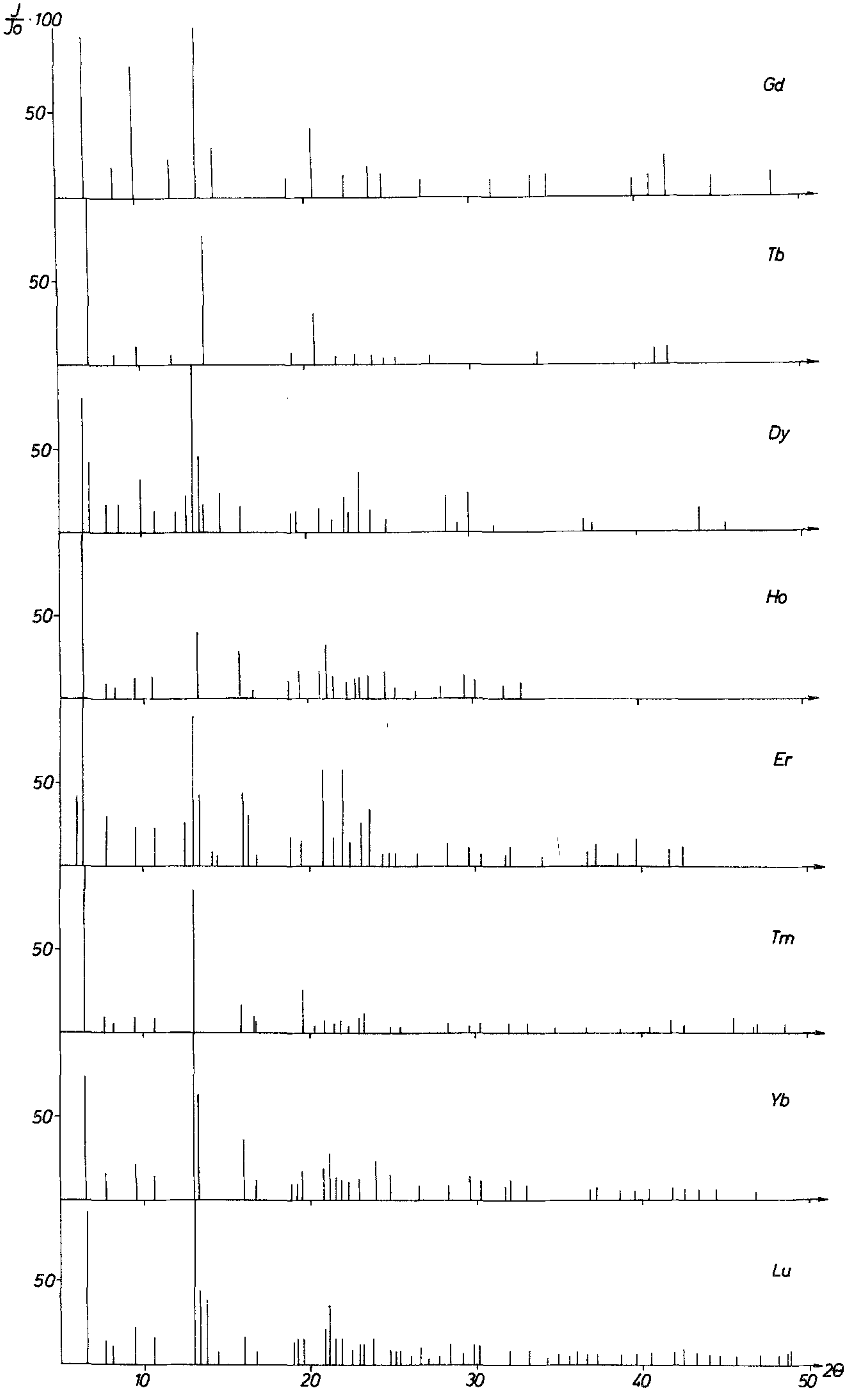

Fig. 2. Radiograms of *p*-nitrobenzoates of heavy lanthanides

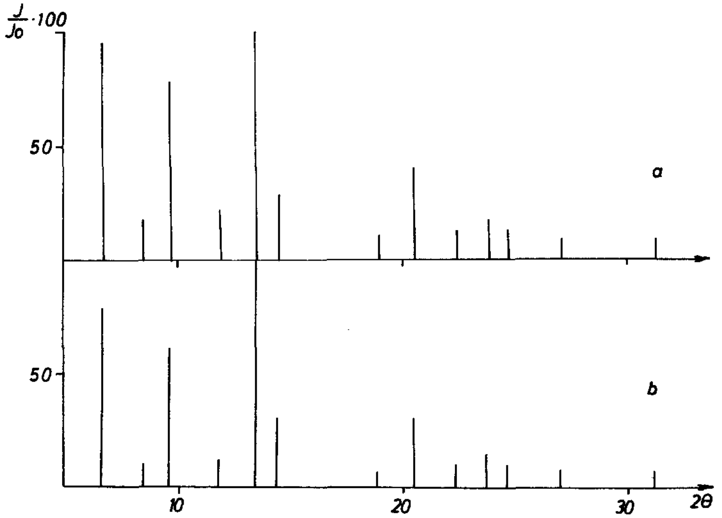

Fig. 3. Comparison of radiograms for *a* hydrated and *b* dehydrated *p*-nitrobenzoate of Gd

anum and lanthanide oxides formed by roasting the oxalates and *p*-nitrobenzoates were recorded. From the obtained results it follows that irrespective of the way of formation of the rare earth element oxide their structures remain the same.

In order to ascertain that during the dehydration process *p*-nitrobenzoates of rare earth elements were not transformed to nitrito complexes, the X-ray spectra for hydrates of *p*-nitrobenzoates and dehydrated complexes were recorded. The obtained results reveal that anhydrous *p*-nitrobenzoates are crystalline compounds having a less degree of crystallinity than the hydrated ones. Taking this fact into account it seems possible to assume that during heating in the temperature range 273–573 K *p*-nitrobenzoates of rare earth elements do not transform to the nitrito complexes and the loss of crystallization water molecules does not modify their crystalline structures (Fig. 3). The hydrates of *p*-nitrobenzoates of Y, La and lanthanides are stable up to 573 K, after which they are explosively decomposed at the melting point. Therefore the thermal decomposition study for these complexes was carried out in the temperature range 273–573 K. The temperature data for dehydration process and the values of dehydration energies determined for these complexes are given in Table 5.

Figures 4 and 5 show the derivatograms of terbium and lutetium *p*-nitrobenzoates, respectively.

Table 5. *Temperature ranges of the dehydration process of* p-*nitrobenzoates of* Y, La, *and lanthanides*

Compound $L = C_7H_4NO_4$	ΔT_1 (K)	Loss of weight %		$n H_2O$	ΔT_2 (K)	Loss of weight %		$n H_2O$	T_{max} (K)	T_k (K)	E (kJ mol^{-1})	
		Calcd.	Found			Calcd.	Found					
$YL_3 \cdot 3H_2O$	353–391	5.61	5.75	2	393–423	8.42	8.59	1	393; 433	433	81.26	123.90
$LaL_3 \cdot 3H_2O$	333–393	5.21	5.25	2	413–453	7.81	7.50	1	393; 453	463	40.83	75.96
$CeL_3 \cdot 3H_2O$	333–393	5.20	5.25	2	413–453	7.80	7.60	1	393; 463	473	60.94	142.10
$PrL_3 \cdot 3H_2O$	353–393	5.19	5.19	2	413–443	7.79	7.50	1	383; 443	463	76.18	97.85
$NdL_3 \cdot 3H_2O$	353–393	5.17	5.05	2	433–463	7.75	7.50	1	383; 463	473	48.13	53.44
$SmL_3 \cdot 3H_2O$	343–383	4.99	4.80	2	423–453	7.49	7.50	1	373; 453	473	60.95	102.32
$EuL_3 \cdot 3H_2O$	333–373	5.11	5.10	2	423–453	7.67	7.50	1	383; 443	453	43.35	102.32
$GdL_3 \cdot 3H_2O$	333–373	5.07	4.95	2	413–443	7.61	7.50	1	373; 443	463	43.25	65.23
$TbL_3 \cdot 3H_2O$	323–383	5.07	5.10	2	387–460	7.59	7.52	1	367; 445	460	62.38	74.77
$DyL_3 \cdot 3H_2O$	329–403	5.03	5.05	2	413–453	7.55	7.30	1	385; 437	461	56.74	67.34
$HoL_3 \cdot 3H_2O$	333–413	7.54	7.40	3	—	—	—	—	387	412	69.65	
$ErL_3 \cdot 3H_2O$	323–443	7.50	7.40	3	—	—	—	—	383	416	57.06	
$TmL_3 \cdot 3H_2O$	323–403	7.48	7.58	3	—	—	—	—	383	417	50.80	
$YbL_3 \cdot 3H_2O$	323–413	7.44	7.48	3	—	—	—	—	377	409	42.72	
$LuL_3 \cdot 3H_2O$	343–413	7.42	7.46	3	—	—	—	—	378	412	40.35	

ΔT_1 Temperature range (K) corresponding to the endothermic loss of two or three molecules of crystallization water
ΔT_2 Temperature range (K) corresponding to the endothermic loss of one molecule crystallization water

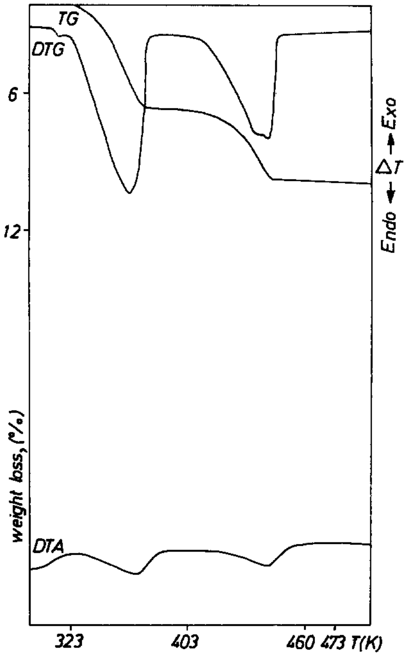

Fig. 4. TG, DTG, and DTA curves of $Tb(C_7H_4NO_4)_3 \cdot 3\,H_2O$

From the obtained results it follows that *p*-nitrobenzoates of rare earth elements are dehydrated in one or two steps.

p-Nitrobenzoates of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy gradually lose two or one molecules of crystallization water in two steps in the temperature range 323–403 K and 387–463 K, respectively. The loss of crystallization water molecules is connected with two strong endothermic effects. The trihydrates of *p*-nitrobenzoates of the remaining rare earth elements (Ho, Er, Tm, Yb, Lu) expel three molecules of crystallization water in one step in the temperature range 323–443 K. Hydrates of *p*-nitrobenzoates of Y, La and lanthanides are stable up to 323–353 K. The least thermally stable complexes are the hydrates of terbium, erbium, thulium and ytterbium which start to lose the crystallization water at 323 K. The more thermally stable complexes are those of dysprosium, gadolinum, europium, cerium and lanthanum which release crystallization water at temperatures 329 and 393 K, respectively. *p*-Nitrobenzoates of Sm and Lu start to dehydrate at 343 K. The most thermally stable compounds are the yttrium and neodymium *p*-nitrobenzoates which start losing crystallization water at 353 K.

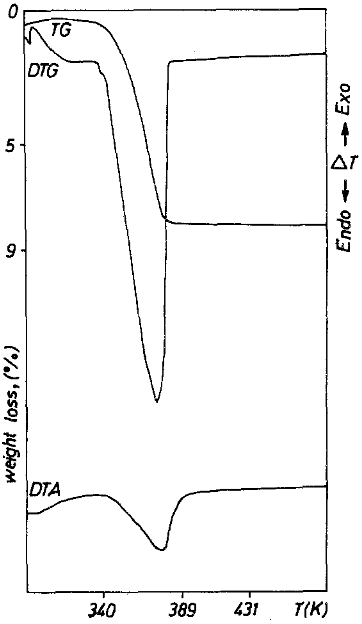

Fig. 5. TG, DTG, and DTA curves of $Lu(C_7H_4NO_4)_3 \cdot 3\,H_2O$

In the temperature range from 409 K (for Yb) to 473 K (for Ce, Nd and Sm) the anhydrous salts of rare earth element p-nitrobenzoates are formed.

Considering the temperature and the course of the dehydration process it is possible to suppose that the molecules of water in p-nitrobenzoates of rare earth elements are similarly bound. The small values of the dehydration temperatures reveal that it is probably outer sphere water. According to the fact that on heating the molecules of crystallization water are gradually lost in one or two steps it is possible to suggest that in p-nitrobenzoates of Y, La and lanthanides they are coordinated to lanthanide ions with different strength. In p-nitrobenzoates of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy the two, more weakly bound molecules of crystallization water are expelled in the temperature range 329–403 K whereas the third one, probably more strongly coordinated to lanthanide ions is released at a temperature range of 387–463 K.

The small values of the dehydration temperature and the loss of three molecules of crystallization water in one step in the case of p-nitrobenzoates of Ho, Er, Tm, Yb and Lu indicate that the water molecules are probably weakly coordinated to Ln^{3+} ions. The trihydrates of *p*-nitrobenzoates of those elements lose the crystallization water molecules in one step while *p*-nitrobenzoates of Y, La and lanthanides prepared by *Khiyalov* and *Musaev* were found to release them in the two steps in the temperature ranges 313–458 K and 338–453 K, respectively [41]. From the thermal analysis data recorded for the trihydrates of *p*-nitrobenzoates of Y, La and lanthanides it follows that the initial temperature of the dehydration process for these complexes does not regularly change with the atomic number of the metallic element. No regular changes of the temperature of the anhydrous salt formations with the lanthanide ionic radii were also observed.

From preliminary studies on the thermal stability of complexes of *p*-nitrobenzoates of Y, La and lanthanides in air atmosphere in the temperature range 273–1 173 K it appears that the decomposition of anhydrous *p*-nitrobenzoates of La, Ce, Pr and Nd leads through oxycarbonates to oxides of those elements whereas the anhydrous *p*-nitrobenzoates of Y, Sm and Gd are directly decomposed to oxides.

From TG and DTA curves the activation energies of dehydration reactions were calculated according to the method of *Fatieev* and *Pletniew* [47].

According to the obtained results presented in Table 5 the values of activation energies do not seem to change smoothly with increasing atomic number of elements. The values of the activation energies of dehydration reactions for *p*-nitrobenzoates of Y, La, Ce, Pr, Nd, Sm, Gd, Tb and Dy connected with the loss of two molecules of crystallization water are smaller compared to those obtained for the loss of the third one in these complexes.

Accordingly, it is possible to suppose that two molecules of outer-sphere water are more weakly bound compared to that for the third one. The values of activation energies of dehydration reactions connected with the loss of three molecules of crystallization water in one step for *p*-nitrobenzoates of Ho, Er, Tm, Yb and Lu are relatively small. In these complexes the crystallization water molecules are similarly bound probably they represent the most weakly coordinated ones compared to those in the remaining complexes of lanthanide ions.

The solubilities of *p*-nitrobenzoates of Y, La and lanthanides in water at 298 K were measured. They are in the order of 10^{-3} mol dm^{-3} (Table 6).

p-Nitrobenzoates of heavy lanthanides are better soluble than those for light ones. The values of solubility of the compounds do not change regularly with the atomic number from La to Lu. The values of solubilities for *p*-nitrobenzoates of Y, La and lanthanides were compared to those

Table 6. *Solubility of* p-*nitrobenzoates of rare earth elements in water at 293 K*

Complex $L = C_7H_4NO_4$	Solubility as anhydrous salt $mol\,dm^{-3} \cdot 10^{-3}$
$YL_3 \cdot 3\,H_2O$	2.83
$LaL_3 \cdot 3\,H_2O$	2.07
$CeL_3 \cdot 3\,H_2O$	1.86
$PrL_3 \cdot 3\,H_2O$	1.75
$NdL_3 \cdot 3\,H_2O$	1.83
$SmL_3 \cdot 3\,H_2O$	1.85
$EuL_3 \cdot 3\,H_2O$	1.97
$GdL_3 \cdot 3\,H_2O$	2.28
$TbL_3 \cdot 3\,H_2O$	2.35
$DyL_3 \cdot 3\,H_2O$	2.36
$HoL_3 \cdot 3\,H_2O$	2.52
$ErL_3 \cdot 3\,H_2O$	2.04
$TmL_3 \cdot 3\,H_2O$	2.06
$YbL_3 \cdot 3\,H_2O$	2.12
$LuL_3 \cdot 3\,H_2O$	2.27

determined for *o*-nitrobenzoates whose solubilities are in the order of $10^{-2}\,mol\,dm^{-3}$. The difference in the values of solubilities in the nitro complexes is caused by a change of properties due to the different position of the NO_2 group in benzene ring.

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