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Preparation and Properties of Yttrium, Lanthanum and Lanthanide *o*-nitrobenzoates

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The conditions of the formation of yttrium, lanthanum and lanthanide *o*-nitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K were determined (their solubilities are of the order of 10^{-2} mol dm^{-3}). The IR and X-ray spectra for the obtained complexes and the dehydrated rare earth element *o*-nitrobenzoates were recorded; all prepared complexes are crystalline compounds. The conditions of thermal decomposition of the complexes were also studied. It was found that on heating above 523 K the complexes decompose explosively and undergo a melting process at the same time. Therefore the thermal decomposition for complexes being studied was carried out in the temperature range 273–523 K. From the results it appears that during the dehydration process or with the increase of temperature no transformation of the nitro group to nitrito occurs.

(Keywords: Complexes; Rare earth elements; Lanthanides; IR)

Darstellung und Eigenschaften von Y, La *und Lanthanidenorthonitrobenzoaten*

Die Bedingungen zur Darstellung von Y-, La- und Lanthanidenorthonitrobenzoaten wurden untersucht. Ihre quantitative Zusammensetzung und ihre Wasserlöslichkeit bei 298 K wurde bestimmt; die Löslichkeit ist in der Größenordnung 10^{-2} mol dm^{-3}. Die Infrarot- und Röntgenspektren der erhaltenen Komplexe sowie der Orthonitrobenzoate 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 festgestellt: sie zerfallen über 523 K explosiv und schmelzen zugleich. Der thermische Zerfall der erhaltenen Orthonitrobenzoate der seltenen Erden wurde im Temperaturbereich von 273—523 K untersucht. Es wurde festgestellt, daß die Y-, La- und Lanthanidenorthonitrobenzoate bei Temperaturzunahme oder im Dehydratisierungsprozeß keiner Umgruppierung in entsprechende Nitritoverbindungen unterliegen.

Introduction

o-nitrobenzoic acid is a yellow, crystalline solid, readily soluble in HCl and in the solutions of organic acids and sparingly soluble in water [1, 2]. Its electrolytic dissociation constant is equal to $6.2 \cdot 10^{-3}$ (25 °C) [1–4]. *o*-Nitrobenzoic acid crystallizes in the triclinic system [1, 5–7] and occurs in dimer form [5]. The values of the dipole moments for *o*-nitrobenzoic acid in benzene and dioxane were determined [8] and its dissociation constant in acetone was also established [9].

The compounds of *o*-nitrobenzoic acid are comparatively little known but a survey of literature shows that it is possible to find papers on its salts with some cations and on the investigations of some of their physical and chemical properties. The following salts of *o*-nitrobenzoic acid with cations: NH_4, Na [1], K [1, 10–12], Rb, Cs [10], Cu [1, 13], Ba [14], Hg [15], Pb [16], Zr and Hf [17], Tl [11, 18], Y, La, Ce [19], Nd, Sm, Gd [20] and W [21] were obtained in solid state. A survey of the literature shows that the investigations are mainly connected with the composition of the compounds, the determination of crystalline structures and solubilities in water and organic solvents, with the investigation of thermal stability in air atmosphere and with the measurements of the magnetic moments and electrolytic conductivity. *o*-nitrobenzoates of Y, La, Ce(III) [19], Nd, Sm, and Gd [20] were obtained as dihydrates with general formula $Ln(C_7H_4NO_4)_3 \cdot 2\,H_2O$. Their solubilities in water and organic solvents were measured; they are readily soluble in water.

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

Experimental

o-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 *o*-nitrobenzoate ($pH \sim 5$) 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 and ethanol until ammonium ions were removed and dried at 303 K to a constant mass. The contents of carbon, hydrogen and nitrogen were determined by elemental analysis with V_2O_5 as oxidizing agent. The rare earth element contents were established by the oxalic method. From the obtained results (Table 1) it follows that *o*-nitrobenzoates of rare earth relements are hydrated salts with a metal to ligand ratio of 1 : 3.

o-Nitrobenzoates of Nd, Sm, Eu(III) and Gd form monohydrates while the remaining ones dihydrates. *o*-Nitrobenzoates of rare earth elements were obtained in crystalline form with yellow colour characteristic for compounds containing nitro groups.

Table 1. *Analytical data*

Compound $L = C_7H_4NO_4$	%H		%C		%N		%M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$YL_3 \cdot 2H_2O$	2.55	2.43	40.26	40.20	6.71	6.62	14.20	14.30
$LaL_3 \cdot 2H_2O$	2.37	2.25	37.44	37.23	6.24	6.32	20.64	20.70
$CeL_3 \cdot 2H_2O$	2.37	2.27	37.38	37.28	6.23	6.27	20.78	20.71
$PrL_3 \cdot 2H_2O$	2.37	2.27	37.33	37.34	6.22	6.12	20.87	20.55
$NdL_3 \cdot H_2O$	2.12	2.12	38.16	37.18	6.36	6.36	21.84	21.69
$SmL_3 \cdot H_2O$	2.10	2.14	37.81	37.82	6.30	6.29	22.56	22.40
$EuL_3 \cdot H_2O$	2.09	2.05	37.72	37.87	6.28	6.30	22.74	22.47
$GdL_3 \cdot H_2O$	2.07	2.02	37.43	37.20	6.23	6.21	23.35	23.29
$TbL_3 \cdot 2H_2O$	2.30	2.26	36.36	36.55	6.06	6.11	22.93	22.86
$DyL_3 \cdot 2H_2O$	2.29	2.17	36.18	36.21	6.03	5.96	23.33	23.34
$HoL_3 \cdot 2H_2O$	2.28	2.19	36.05	36.00	6.00	6.12	23.59	23.39
$ErL_3 \cdot 2H_2O$	2.28	2.18	35.93	35.80	5.98	6.01	23.85	23.89
$TmL_3 \cdot 2H_2O$	2.27	2.20	35.82	35.62	5.97	5.99	24.07	24.06
$YbL_3 \cdot 2H_2O$	2.26	2.22	35.64	35.44	5.94	6.00	24.47	24.26
$LuL_3 \cdot 2H_2O$	2.25	2.17	35.54	35.24	5.92	5.82	24.67	24.95

In order to confirm the chemical composition of the obtained salts, IR spectra for the prepared complexes, the spectra for *o*-nitrobenzoic acid, sodium *o*-nitrobenzoate, for the dehydrated *o*-nitrobenzoates of yttrium, lanthanum and lanthanides and also 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 *o*-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 CuK_α radiation. The measurements were made within the range $2Q = 4$–$80°$ by means of the *Debye-Scherrer* method.

The thermal stability of the complexes was studied by the use of TG, DTA and DTG techniques. The measurements were made with a Q—1 500 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 *o*-nitrobenzoates of yttrium, lanthanum and lanthanides are presented.

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

Results and Discussion

The prepared complexes were found to be mono or dihydrates having formula: $Ln(C_7H_4NO_4)_3 \cdot nH_2O$, where: Ln = Y, La, Ce—Lu; $n = 1$ for Nd, Sm, Eu, Gd; $n = 2$ for Y, La, Ce, Pr, Tb, Dy, Ho, Er, Tm, Yb, Lu. The

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

Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Assignments
3 380	3 380	3 380	3 380	3 380	3 380	3 380	3 360	stretching vibration of OH of HOH
1 590	1 590	1 590	1 590	1 580	1 590	1 590	1 590	asymmetrical vibration of COO^-
1 530	1 530	1 540	1 540	1 535	1 530	1 540	1 545	asymmetrical vibration of NO_2
1 490	1 495	1 495	1 490	1 490	1 495	1 500	1 500	ring vibration (ortho-substituted benzene ring)
1 430	1 420	1 420	1 420	1 420	1 420	1 430	1 430	symmetrical vibration of COO^-
1 359	1 350	1 350	1 350	1 345	1 350	1 355	1 355	symmetrical vibration of NO_2
850	850	850	850	850	850	850	850	stretching vibration of C—N
760	760	760	760	760	760	785	760	vibrations of the neighbouring hydrogen atoms in the benzene ring
655	650	655	655	655	650	655	655	wagging vibration of NO_2
540	550	540	540	540	550	545	545	out-of-plane deformation vibration of C—H
445	445	445	445	445	445	445	445	stretching vibration of the metal-oxygen bond

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

Tb	Dy	Ho	Er	Tm	Yb	Lu	Assignments
3 360	3 360	3 360	3 360	3 380	3 380	3 380	stretching vibration of OH of HOH
1 595	1 595	1 595	1 595	1 595	1 590	1 590	asymmetrical vibration of COO^-
1 540	1 545	1 550	1 550	1 540	1 530	1 530	asymmetrical vibration of NO_2
1 500	1 500	1 500	1 500	1 490	1 490	1 490	ring vibrations for ortho-substituted benzene ring
1 430	1 430	1 430	1 440	1 430	1 430	1 430	symmetrical vibration of COO^-
1 355	1 355	1 355	1 350	1 360	1 350	1 350	symmetrical vibration of NO_2
850	850	850	850	850	850	850	stretching vibration of C—N
760	760	760	760	740	740	760	vibrations of the neighbouring hydrogen atoms in the benzene ring
655	655	655	655	650	655	655	wagging vibration of NO_2
545	545	545	545	560	540	540	out-of-plane deformation vibration of C—H
445	445	445	445	440	445	445	stretching vibration of metal-oxygen bond

hydration degree for the complexes is not regularly changing with the decrease of the ionic radius in the lanthanide series.

The infrared spectra for *o*-nitrobenzoic acid show the following absorption bands: sharp absorption band of OH group between 3 600–2 800 cm^{-1}, a strong band of COOH at 1 680 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of the NO_2 group occuring at 1 530 cm^{-1} and 1 350 cm^{-1} respectively, the C—OH absorption band at around 1 410 cm^{-1}, the deformation vibration bands of the aromatic ring at 1 150 cm^{-1}, the band at 920 cm^{-1} arising from out-of-plane deformation vibration of the O—H group, a band at 860 cm^{-1} due to C—N stretching vibration and the bands confirming the neighbouring hydrogen atom vibrations in the benzene ring substituted in 1 : 2 position at 780 cm^{-1} and 730 cm^{-1} respectively. The band at around 655–650 cm^{-1} indicates the wagging vibrations of NO_2 group and the band at 540 cm^{-1} is indicative of out-of-plane C—H vibrations.

When the acid is converted to the salt a change in the spectra is observed. The absorption band at 1 680 cm^{-1} characteristic for COOH disappears which is indicative for free —COOH groups in the complexes. The IR spectra for all *o*-nitrobenzoates are quite similar and their analysis confirms the formulations of *o*-nitrobenzoates obtained as nitro complexes.

In the IR spectra of the rare earth element *o*-nitrobenzoates the intense broad absorption bands at 3 600–3 100 cm^{-1} confirming the presence of crystallization water molecules coordinated in the complexes are observed. The bands arising from asymmetric vibration of the COO^- group appear at 1 595–1 580 cm^{-1} and 1 440–1 420 cm^{-1}, respectively. The bands occuring at 1 550–1 530 cm^{-1} are assigned to asymmetric and symmetric vibrations of NO_2 group, respectively. The wagging vibrations of NO_2 group occur at 650 cm^{-1}. The absorption bands at 445 cm^{-1} confirm the ionic bond of metal—oxygen. For all *o*-nitrobenzoates of yttrium, lanthanum and lanthanides, no shift changes of these bands are observed. Accordingly, it is possible to suggest that *o*-nitrobenzoic acid forms with rare earth elements complexes having the similar stabilities. In this case the comparison of the stabilities of *o*-nitrobenzoates is possible since these complexes are of the same type.

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

The magnitudes of separation $\Delta\nu$ between the frequencies due to ν_{asym} OCO and ν_{sym} OCO in the complexes are lower than in the sodium salt, which indicates a smaller degree of ionic bond in these complexes

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

Complex $L = C_7H_4NO_4$	ν_{asym} OCO cm^{-1}	ν_{sym} OCO cm^{-1}	$\Delta\nu$
$YL_3 \cdot 2H_2O$	1 590	1 430	160
$LaL_3 \cdot 2H_2O$	1 590	1 420	170
$CeL_3 \cdot 2H_2O$	1 590	1 420	170
$PrL_3 \cdot 2H_2O$	1 590	1 420	170
$NdL_3 \cdot H_2O$	1 590	1 420	170
$SmL_3 \cdot H_2O$	1 590	1 420	170
$EuL_3 \cdot H_2O$	1 590	1 420	170
$GdL_3 \cdot H_2O$	1 590	1 430	160
$TbL_3 \cdot 2H_2O$	1 595	1 430	165
$DyL_3 \cdot 2H_2O$	1 595	1 430	165
$HoL_3 \cdot 2H_2O$	1 595	1 430	165
$ErL_3 \cdot 2H_2O$	1 595	1 440	155
$TmL_3 \cdot 2H_2O$	1 595	1 430	165
$YbL_3 \cdot 2H_2O$	1 590	1 430	160
$LuL_3 \cdot 2H_2O$	1 590	1 430	160
NaL	1 595	1 400	195

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 $\Delta\nu$ 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. *o*-Nitrobenzoates of light lanthanides appear to have a larger $\Delta\nu$ compared to *o*-nitrobenzoates of those rare earth elements whose ionic radii are smaller compared to that for La, Ce, Pr, Nd, Sm, or Eu.

The displacements in the positions of ν_{asym} (NO_2) and ν_{sym} (NO_2) bands for *o*-nitrobenzoates of rare earth elements relative to those in *o*-nitrobenzoic acid are indicative of the coordination of the NO_2 group to lanthanide ions.

In IR spectra of *o*-nitrobenzoates of yttrium, lanthanum and lanthanides the directions of shifts in the frequencies due to ν_{asym} OCO are lower or almost the same as those in the case of sodium *o*-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 for *o*-nitrobenzoates of rare earth elements it appears that on heating above 523 K the obtained complexes are explosively decomposed, simultaneously undergoing the melting process. 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 the endothermic effect) may proceed [22].

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 [23]. As monodentate ligand the nitrite ion may bond either through nitrogen, forming a 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 ν_{asym} (NO_2) and ν_{sym} (NO_2) from the free ion values of $\sim$ 1 328 cm^{-1} and 1 260 cm^{-1}, respectively [24]. In order to verify if the obtained rare earth element *o*-nitrobenzoates do not transform into nitrito isomers during precipitation or during heating to 523 K, the IR spectra for hydrates of *o*-nitrobenzoates of Y, La and lanthanides, for the dehydrated complexes of rare earth element *o*-nitrobenzoates and for sodium nitrite were recorded. The results obtained from their analysis reveal that the *o*-nitrobenzoates of rare earth elements precipitated as solid nitro complexes since in the IR spectra of the complexes the frequencies of absorption bands due to ν_{asym} (NO_2) and ν_{sym} (NO_2) occuring 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 *o*-nitrobenzoates of rare earth elements show that no transformation process of the nitro group to nitrito takes place with rising temperature.

In the IR spectra obtained for all dehydrated *o*-nitrobenzoates of Y, La and lanthanides the absorption bands at 3 600–3 100 cm^{-1} disappear, which indicates the absence of crystallization water molecules in the dehydrated complexes.

No bands confirming the coordination of nitro groups through the oxygen atom are observed since the frequencies of bands due to ν_{asym} (NO_2) and ν_{sym} (NO_2) occur in the same frequency range as in the case of *o*-nitrobenzoates of Y, La and lanthanides not being dehydrated and coordination via oxygen would be expected to raise the frequency of ν_{asym} (NO_2) and to lower that of ν_{sym} (NO_2), respectively, in comparison to those for free NO_2^- ion [24].

The remaining bands in the IR spectra for the dehydrated complexes remain unchanged with regard to those characteristic bands occuring in the same groups as presented for *o*-nitrobenzoates of rare earth elements.

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

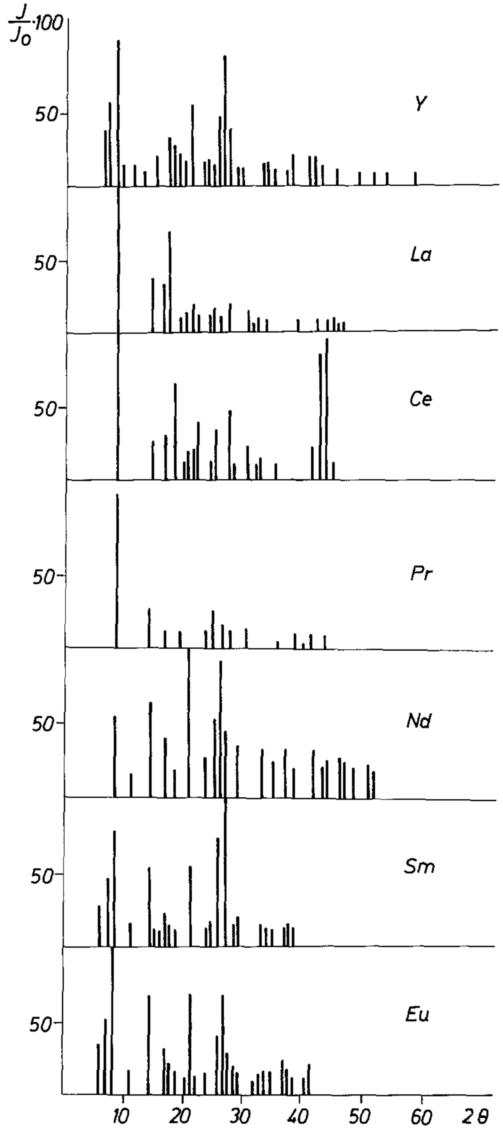

Fig. 1. Radiograms of o-nitrobenzoates of Y, La and light lanthanides

compounds characterizied by low symmetry, large sizes of the unit cells, different structure and various degree of crystallinity (Figs. 1, 2). o-Nitrobenzoates of light lanthanides are characterized by a less degree of crystallinity than o-nitrobenzoates of heavy lanthanides.

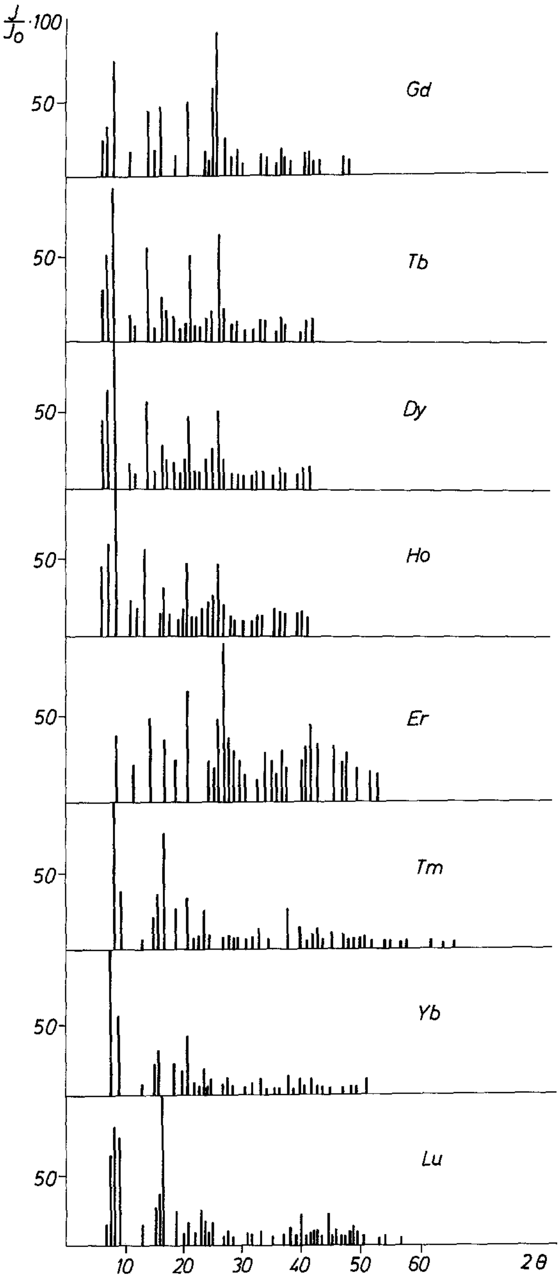

Fig. 2. Radiograms of *o*-nitrobenzoates of heavy lanthanides

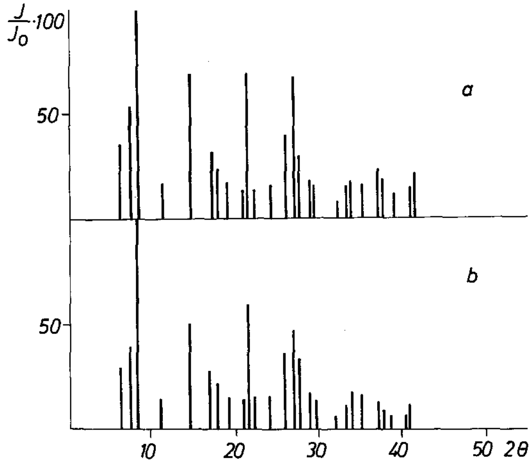

Fig. 3. Comparison of radiograms for *a* hydrated and *b* dehydrated *o*-nitrobenzoate of Eu

o-Nitrobenzoates of Tb, Dy and Ho appear to be isostructural, while *o*-nitrobenzoates of the remaining ones not do reveal such properties.

During slow heating in air, *o*-nitrobenzoates of Y, La and lanthanides form 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, lanthanum and lanthanide oxides obtained by roasting the oxalates and the *o*-nitrobenzoates were recorded. On the basis of the obtained diffractograms the structures of all rare earth element oxides were found to remain the same irrespective of the way of their formation.

To make clear if during the dehydration process of *o*-nitrobenzoates the transformation of the nitro group to nitrito takes place, the X-ray spectra for hydrates of *o*-nitrobenzoates and dehydrated complexes were recorded. From their analysis it follows that anhydrous *o*-nitrobenzoates are crystalline compounds and have a less degree of crystallinity than the hydrated ones. No changes of their structures in comparison to the hydrated salts were observed. Considering this fact it is possible to assume that during the dehydration process in the temperature range 273–523 K *o*-nitrobenzoates of rare earth elements are not converted to nitrito complexes and the loss of crystallization water molecules does not modify their crystalline structures (Fig. 3).

Taking into account the great thermal instability of *o*-nitrobenzoates of Y, La and lanthanides above 523 K because of their explosive decomposition in connection with the melting process, their thermal

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

Compound $L = C_7H_4NO_4$	ΔT_1	Loss of weight		nH$_2$O	ΔT_2	Loss of weight		nH$_2$O	T_{max} DTA	T_k K
		Calcd.	Found			Calcd.	Found			
$YL_3 \cdot 2H_2O$	358–380	2.87	2.80	1	389–461	5.75	5.80	1	374, 421	475
$LaL_3 \cdot 2H_2O$	347–395	2.67	2.57	1	397–445	5.34	5.14	1	386, 426	461
$CeL_3 \cdot 2H_2O$	344–392	2.74	2.68	1	392–428	5.34	5.36	1	372, 422	448
$PrL_3 \cdot 2H_2O$	336–395	2.66	2.60	1	397–463	5.33	5.28	1	368, 421	463
$NdL_3 \cdot H_2O$	—	—	—	—	426–489	2.72	2.90	1	459	489
$SmL_3 \cdot H_2O$	—	—	—	—	417–484	2.70	2.68	1	444	484
$EuL_3 \cdot H_2O$	—	—	—		421–486	2.69	2.83	1	452	486
$GdL_3 \cdot H_2O$	—	—	—	—	411–477	2.67	2.72	1	438	477
$TbL_3 \cdot 2H_2O$	—	—	—	—	405–497	5.19	5.00	2	445	493
$DyL_3 \cdot 2H_2O$	—	—	—	—	401–497	5.16	5.20	2	431	497
$HoL_3 \cdot 2H_2O$	—	—	—	—	393–491	5.15	4.95	2	433	491
$ErL_3 \cdot 2H_2O$	—	—	—	—	397–472	5.13	5.00	2	422	472
$TmL_3 \cdot 2H_2O$	—	—	—	—	343–453	5.11	4.98	2	387	473
$YbL_3 \cdot 2H_2O$	—	—	—	—	317–435	5.09	4.87	2	377	435
$LuL_3 \cdot 2H_2O$	—	—	—	—	323–427	5.07	5.10	2	381	475

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

stability was studied in the temperature range 273–523 K. The obtained results collected in Table 5 show that *o*-nitrobenzoates of rare earth elements are dehydrated in one or two steps. Dihydrates of Y, La, Ce(III) and Pr(III) gradually lose water in two steps in the temperature ranges 336–395 K and 389–463 K respectively. The removal of crystallization water molecules is connected with two strong endothermic effects. On heating the monohydrates of Nd, Sm, Eu(III) and Gd and the dihydrates of heavy lanthanides expel the molecules of crystallization water in one step. Hydrates of *o*-nitrobenzoates Y, La and lanthanides are stable up to 317–426 K. The least thermically stable complexes are the hydrates of ytterbium and lutetium which start to lose the crystallization water at 317 and 323 K, respectively. The more thermically stable complexes of Y, La, Ce(III), Pr(III), Ho, Er, Tm release crystallization water at a temperature below 400 K. Complexes of Sm, Eu, Gd, Tb and Dy start to dehydrate at temperature above 400 K. The most thermically stable compound is the *o*-nitrobenzoate of Nd which starts losing crystallization water at a temperature of 426 K.

In the temperature range from 435 K (for Yb) to 497 K (for Dy) the anhydrous salts of rare earth elements are formed.

Considering the temperature and the course of the dehydration process it is possible to suppose that the molecules of water in *o*-nitrobenzoates of Y, La and lanthanides are similarly bound. The small

Table 6. *Solubility of o-nitrobenzoates of yttrium, lanthanum and lanthanides in water at 293 K*

Complex $L = C_7H_4NO_4$	Solubility as anhydrous salt $mol\,dm^{-3} \cdot 10^{-2}$
$YL_3 \cdot 2\,H_2O$	4.3
$LaL_3 \cdot 2\,H_2O$	4.6
$CeL_3 \cdot 2\,H_2O$	4.3
$PrL_3 \cdot 2\,H_2O$	3.9
$NdL_3 \cdot H_2O$	2.7
$SmL_3 \cdot H_2O$	2.4
$EuL_3 \cdot H_2O$	2.1
$GdL_3 \cdot H_2O$	2.4
$TbL_3 \cdot 2\,H_2O$	2.6
$DyL_3 \cdot 2\,H_2O$	2.5
$HoL_3 \cdot 2\,H_2O$	2.6
$ErL_3 \cdot 2\,H_2O$	3.2
$TmL_3 \cdot 2\,H_2O$	5.7
$YbL_3 \cdot 2\,H_2O$	4.3
$LuL_3 \cdot 2\,H_2O$	6.9

values of the dehydration temperatures show that it is probably outer sphere water.

The initial temperature of the dehydration process does not regularly change with the atomic number of the metallic element.

The solubilities of *o*-nitrobenzoates of Y, La and lanthanides in water at 298 K were measured. They are in the order of 10^{-2} mol dm^{-3} (Table 6). The *o*-nitrobenzoate of Lu is the most soluble salt whereas europium *o*-nitrobenzoate the least soluble one. The values of solubilities of the compounds do not change smoothly with the atomic number from La to Lu.

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