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Preparation and Properties of Yttrium, Lanthanum and Lanthanide 2,4-Dinitrobenzoates

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Summary. The conditions of the formation of rare earth 2,4-dinitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K determined (their solubilities are of the order of 10^{-2} mol dm^{-2}). The IR and X-ray spectra for the hydrated and dehydrated complexes were recorded. All complexes are crystalline compounds. The condition of thermal decomposition of the complexes were also investigated. On heating above 573 K the complexes were found to decompose explosively and undergo a melting process at the same time. Accordingly, the thermal decomposition for the complexes was carried out in the temperature range 273–573 K. The thermal stability data reveal them to dehydrate in one step and the crystallization water molecules to be bound in various ways. From the obtained results it appears that during the dehydration process no isomerisation of the nitro group to nitrito occurs.

Keywords. Yttrium; Lanthanum; Lanthanide 2,4-dinitrobenzoates.

Herstellung und Eigenschaften von Y-, La- und Lanthaniden-2,4-Dinitrobenzoaten

Zusammenfassung. Die Bedingungen zur Darstellung von Y-, La-, und Lanthaniden-2,4-dinitrobenzoaten wurden untersucht. Ihre quantitative Zusammensetzung und ihre Wasserlöslichkeit bei 298 K wurden bestimmt (die Löslichkeit ist in der Größenordnung 10^{-2} mol dm^{-3}). Die Infrarot- und Röntgenspektren der erhaltenen Komplexe sowie der dehydratisierten wurden gemessen und dabei festgestellt, daß es sich um kristalline Verbindungen handelt. Das thermische Verhalten der Komplexe wurde ebenfalls untersucht: sie zerfallen über 573 K explosiv und schmelzen zugleich. Der thermische Zerfall der 2,4-Dinitrobenzoate wurde im Temperaturbereich von 273–573 K untersucht. Aus der thermischen Analyse ergibt sich, daß die Komplexe und die Kristallwassermoleküle in einer Stufe dehydratisiert werden und verschiedenartig gebunden sind. Es wurde festgestellt, daß die Y-, La-, und Lanthaniden-2,4-Dinitrobenzoate bei Temperaturzunahme oder im Dehydratisierungsprozeß keiner Umgruppierung in entsprechenden Nitritoverbindungen unterliegen.

Introduction

2,4-Dinitrobenzoic acid is a yellow, crystalline solid, readily soluble in hot water but sparingly soluble in cold one [1]. It crystallizes in the monoclinic system and occurs in dimer form [1–4]. Its electrolytic dissociation constants are equal to $3.85 \cdot 10^{-2}$ ($t = 25\,^{\circ}\mathrm{C}$) and $3.2 \cdot 10^{-2}$ ($t = 40\,^{\circ}\mathrm{C}$). The compounds of 2,4-dinitrobenzoic acid are comparatively little known. From a survey of the literature it follows that it is possible to find some papers on its salts with the following cations: Na, Mg, Ca, Ba [1], NH_4, K and Pb(II) [5, 6].

The aim of this work was to obtain in solid state the 2,4-dinitrobenzoates of yttrium, lanthanum and lanthanides, not being obtained till now, with a metal to ligand ratio of 1 : 3 and to examine some of their properties.

Experimental

2,4-Dinitrobenzoates of yttrium, lanthanum and lanthanides were prepared by adding the equivalent quantities of 0.2 *M* ammonium 2,4-dinitrobenzoate ($pH \sim 5$) to a hot solution containing the rare earth element nitrates and crystallizing at 293 K.

The solids formed were filtered off, washed with 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 oxalate method (Table 1). The content of crystallization water molecules were determined from the curve of TG and by isothermal heating at 573 K.

The IR spectra for the complexes, the spectra for 2,4-dinitrobenzoic acid, sodium 2,4-dinitrobenzoate and dehydrated 2,4-dinitrobenzoates of yttrium, lanthanum and lanthanides and for sodium nitrite were recorded as KBr discs on a UR-20 spectrophotometer (range 4 000–400 cm^{-1}). Some of the experimental data are presented in Table 2.

The X-ray diffraction patterns for hydrated and dehydrated rare earth element 2,4-dinitrobenzoates and lanthanide oxides obtained from the ignition of the oxalates and 2,4-dinitrobenzoates of yttrium, lanthanum and lanthanides were taken on a DRON-2 diffractometer using Ni filtered CuKα radiation. The measurements were made within the range $2\,Q = 4$–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 of 200 mg were heated at a sensitivity TG − 50 mg, DTG − 500 µV, DTA − 500 µV (Table 3).

The solubilities of 2,4-dinitrobenzoates of yttrium, lanthanum and lanthanides in water at 298 K were determined by measuring the concentration of Ln^{3+} ions in saturated solutions by the oxalate method (Table 3).

Results and Discussion

2,4-Dinitrobenzoates of yttrium, lantanum, and lanthanides were obtained in crystalline form with yellow colour and a metal to ligand ratio of 1 : 3 of the general formula: $Ln(C_7H_3O_6N_2)_3 \cdot 2\,H_2O$; where Ln = Y, La, Ce − Lu.

The compounds were characterized by their elemental analyses (Table 1) and IR spectra, which confirmed their formulations as nitro complexes. The IR spectra for all rare earth element 2,4-dinitrobenzoates are similar. When the acid is converted into the salt the absorption band of the COOH group at 1 730 cm^{-1} disappears and two bands arising from asymmetric and symmetric vibrations of COO$^-$ appear at 1 605–1 580 cm^{-1} and 1 430–1 405 cm^{-1}, respectively. The broad absorption bands with the maxima at 3 520–3 420 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands occuring at 1 550–1 540 cm^{-1} and 1 355–1 350 cm^{-1} are assigned to asymmetric and symmetric vibration of NO_2 groups, respectively. The stretching vibrations of the C = C bands of benzene appear at 1 490–1 485 cm^{-1}. The bands at 1 065–1 060 cm^{-1} are indicative of vibrations of the neighbouring hydrogen atoms in aromatic ring substituted in 1, 2, 4 positions. The bands arising from out-of-plane deformation vibrations of the C–H group occur at 925 cm^{-1} and bands due to metal − oxygen bond are

Table 1. Analytical data

Complex $L = C_7H_3O_6N_2$	% C		% N		% H		% Me	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\mathrm{Y}L_3 \cdot 2\,\mathrm{H_2O}$	33.24	33.14	11.08	11.15	1.71	1.81	10.69	10.76
$\mathrm{La}L_3 \cdot 2\,\mathrm{H_2O}$	31.19	31.08	10.39	10.27	1.60	1.50	17.08	16.98
$\mathrm{Ce}L_3 \cdot 2\,\mathrm{H_2O}$	31.14	31.03	10.38	10.28	1.60	1.72	17.31	17.24
$\mathrm{Pr}L_3 \cdot 2\,\mathrm{H_2O}$	31.11	31.13	10.37	10.20	1.60	1.71	17.39	17.42
$\mathrm{Nd}L_3 \cdot 2\,\mathrm{H_2O}$	30.98	31.00	10.32	10.24	1.59	1.63	17.73	17.70
$\mathrm{Sm}L_3 \cdot 2\,\mathrm{H_2O}$	30.76	30.61	10.25	10.15	1.58	1.79	18.35	18.27
$\mathrm{Eu}L_3 \cdot 2\,\mathrm{H_2O}$	30.69	30.81	10.23	10.38	1.58	1.65	18.51	18.59
$\mathrm{Gd}L_3 \cdot 2\,\mathrm{H_2O}$	30.49	30.26	10.16	10.06	1.57	1.41	19.03	19.16
$\mathrm{Tb}L_3 \cdot 2\,\mathrm{H_2O}$	30.43	30.33	10.14	10.15	1.50	1.56	19.19	19.19
$\mathrm{Dy}L_3 \cdot 2\,\mathrm{H_2O}$	29.04	29.09	9.68	9.68	1.26	1.27	18.73	18.25
$\mathrm{Ho}L_3 \cdot 2\,\mathrm{H_2O}$	30.21	30.33	10.07	10.04	1.50	1.63	19.77	20.04
$\mathrm{Er}L_3 \cdot 2\,\mathrm{H_2O}$	30.13	30.09	10.04	10.14	1.55	1.65	20.00	19.98
$\mathrm{Tm}L_3 \cdot 2\,\mathrm{H_2O}$	30.05	29.96	10.01	9.99	1.55	1.66	20.19	20.02
$\mathrm{Yb}L_3 \cdot 2\,\mathrm{H_2O}$	29.92	30.01	9.97	9.91	1.54	1.64	20.55	20.45
$\mathrm{Lu}L_3 \cdot 2\,\mathrm{H_2O}$	29.85	29.94	9.95	9.91	1.54	1.53	20.73	20.49

observed at 495–470 cm^{-1}. The shift changes of these bands from La to Lu to higher frequencies are probably due to the increasing stability of the M–O bond with increasing atomic number and ionic potential of the element (Table 2).

The values $\Delta\nu$ between the frequencies due to ν_{asym} OCO and ν_{sym} OCO in these complexes are lower than in the sodium salt, which indicates a smaller degree of ionic bond in the complexes compared to that of sodium (Table 2). Having a greater ionic potential than sodium ion, lanthanide ions influence the ligand more strongly, causing its greater deformation. The directions of shifts in the frequencies of these bands are lower (or remain almost the same) and higher, respectively, relative to those in sodium 2,4-dinitrobenzoate. Therefore, the carboxylate ion is supposed to be a bidentate chelating ligand but probably with incomplete equalization of its bond lengths. In the La – Lu series these bond lengths become presumably more equal because the metal – ligand bonding becomes increasingly covalent, which may be indicated by the smaller differences between ν_{asym} OCO and ν_{sym} OCO.

Being greater for light lanthanide ions than for heavy ones, the f-electrons become more concentrated in the series from La – Lu causing the increase of bond covalency in the heavy lanthanides. From the values of $\Delta\nu$ 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. The spectra of the heavy lanthanide complexes characterized by relatively more intense aromatic bands, as compared with light lanthanides, are closer to the spectrum of 2,4-dinitrobenzoic acid. This being connected with an increase in covalency and the degree of delocalization of bond in the heavy lanthanides leads probably to the increase of the decolalization of π electrons and the intensity of the aromatic bands of the $\nu\mathrm{C{=}C}$ bonds of the benzene ring.

Table 2. Frequencies of absorption bands of the COO^- ion and the NO_2 group for Na, Y, La and lanthanide 2,4-dinitrobenzoates and 2,4-dinitrobenzoic acid (cm^{-1})

Compound $L = C_7H_3O_6N_2$	$\nu_{as}OCO$	$\nu_{sym}OCO$	$\Delta\nu$	$\nu_{as}(NO_2)$	$\nu_{sym}(NO_2)$	$\Delta\nu(NO_2)$	ν_{M-O}
$YL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	485
$LaL_3 \cdot 2H_2O$	1610	1410	200	1555	1355	200	470
$CeL_3 \cdot 2H_2O$	1600	1410	190	1550	1350	200	470
$PrL_3 \cdot 2H_2O$	1600	1415	185	1550	1350	200	470
$NdL_3 \cdot 2H_2O$	1605	1420	185	1540	1350	190	475
$SmL_3 \cdot 2H_2O$	1605	1420	185	1550	1360	190	475
$EuL_3 \cdot 2H_2O$	1600	1420	180	1540	1350	190	475
$GdL_3 \cdot 2H_2O$	1595	1420	170	1540	1350	190	475
$TbL_3 \cdot 2H_2O$	1595	1425	170	1550	1350	200	480
$DyL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	480
$HoL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	485
$ErL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	485
$TmL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	485
$YbL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	490
$LuL_3 \cdot 2H_2O$	1600	1430	170	1550	1350	200	495
NaL	1640	1400	240	1540	1350	190	–
HL	–	–	–	1540	1350	190	–

Probably a greater symmetrization of the COO group structure for heavy lanthanide 2,4-dinitrobenzoates is connected with an increase in covalency of bonds and accompanied by a recovery of the aromatic system, reflected in the spectrum by the appearance of the $\nu(C=C)_{ar}$ bands. The relatively lower intensities of the aromatic bands for 2,4-dinitrobenzoates of Y, La and lanthanides compared to those for 2,4-dinitrobenzoic acid indicate the weak interaction of the benzene ring with lanthanide ions. The small values of the displacements in the position of ν_{asym} (NO_2) and ν_{sym} (NO_2) bands for 2,4-dinitrobenzoates of rare earth elements (or their lack) relative to those in 2,4-dinitrobenzoic acid (Table 2) are indicative of the only weak interaction of NO_2 groups with lanthanide ions. To verify that the obtained rare earth element 2,4-dinitrobenzoates do not undergo isomerization (during precipitation or on heating to 573 K [7–9]) the IR spectra for hydrated and dehydrated 2,4-dinitrobenzoates of Y, La and lanthanides and for sodium nitrate were studied. The results reveal that the 2,4-dinitrobenzoates of rare earth elements isolated as solid form nitro complexes and no isomerization of the nitro group to nitrito takes place with rising temperature. The intensities of the aromatic bands in the hydrated complexes are greater than in the dehydrated ones. Probably, the water molecules in the hydrates decrease the metal – ligand interaction causing the decrease of the deformation of electron cloud in the ring and the increase of the intensity of aromatic bands in the dihydrated complexes.

From the diffractogram analysis the hydrated and dehydrated 2,4-dinitrobenzoates of rare earth elements were found to be crystalline compounds characterized by low symmetry, large size of unit cells, different structures and different degrees

Table 3. Temperature ranges of the dehydration process, activation energy of the dehydration reaction and solubility in water (293 K) of 2,4-dinitrobenzoates of Y, La and lanthanides [ΔT_1 (K) = temperature range of dehydration process, n = the number of crystallization water molecules being lost in one endothermic step, T_{max}(K) = temperature of the maximum of the endothermic effect in the DTA curve, T_k(K) = temperature of the anhydrous salt formation]

Complex $L = C_7H_3O_6N_2$	ΔT_1 (K)	Loss of weight		$n$$H_2O$	T_{max}(K)	T_k(K)	E(kJ mol^{-1})	Solubility as anhydrous salt mol dm^{-3} · 10^{-2}
		Calcd.	Found					
YL_3 · 2 H_2O	435–493	4.74	4.70	2	482	511	61	3.83
LaL_3 · 2 H_2O	355–419	4.45	4.50	2	388	432	15	7.05
CeL_3 · 2 H_2O	319–409	4.44	4.39	2	388	413	13	6.20
PrL_3 · 2 H_2O	331–413	4.44	4.42	2	401	425	13	1.87
NdL_3 · 2 H_2O	353–421	4.42	4.38	2	401	426	22	1.22
SmL_3 · 2 H_2O	355–416	4.39	4.40	2	404	429	23	7.89
EuL_3 · 2 H_2O	347–419	4.38	4.40	2	402	432	25	9.00
GdL_3 · 2 H_2O	448–505	4.35	4.30	2	479	513	47	3.60
TbL_3 · 2 H_2O	447–504	4.30	4.28	2	498	513	53	3.60
DyL_3 · 2 H_2O	449–503	4.32	4.30	2	485	513	51	2.22
HoL_3 · 2 H_2O	451–503	4.31	4.28	2	489	515	50	1.63
ErL_3 · 2 H_2O	462–503	4.30	4.38	2	491	515	35	2.00
TmL_3 · 2 H_2O	447–491	4.29	4.26	2	487	512	36	2.60
YbL_3 · 2 H_2O	434–491	4.27	4.29	2	478	508	34	1.50
LuL_3 · 2 H_2O	427–491	4.26	4.24	2	477	503	42	1.03

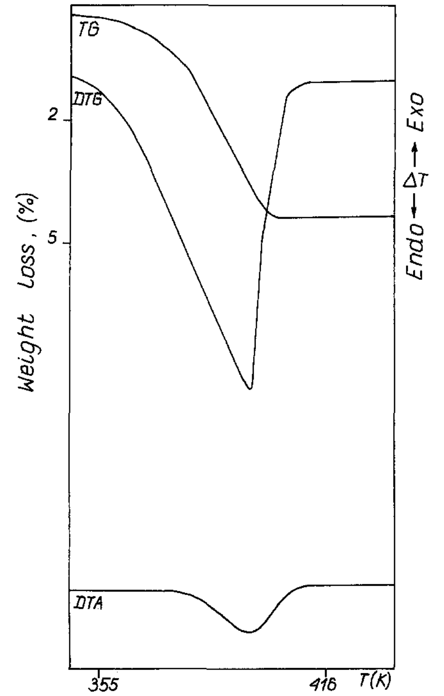

Fig. 1. TG, DTG and DTA curves of $Sm(C_7H_3O_6N_2)_3 \cdot 2\,H_2O$

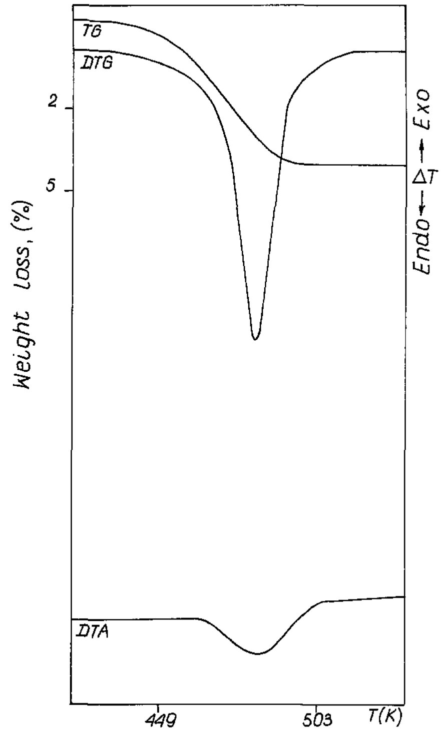

Fig. 2. TG, DTG and DTA curves of $Dy(C_7H_3O_6N_2)_3 \cdot 2\,H_2O$

of crystallinity. The anhydrous 2,4-dinitrobenzoates appear to have a less degree of crystallinity than the hydrated ones.

No changes of their structures compared to the hydrated salts were observed. Accordingly, it is possible to assume that being heated in the temperature range 273–573 K all 2,4-dinitrobenzoates of rare earths do not form the nitrito complexes and the loss of crystallization water molecules does not modify their crystalline structures.

The structures of all rare earth element oxides stay the same irrespective of the way of their formation (by roasting oxalates or 2,4-dinitrobenzoates of Y, La and lanthanides). 2,4-Dinitrobenzoates of Y, La and lanthanides are stable up to 573 K, after which they are explosively decomposed at the melting point.

Thus, their thermal stability was studied only in the temperature range 273–573 K. The temperature data for dehydration process and the values of dehydration energies determined for all dihydrates are presented in Table 3. Figures 1 and 2 exhibit the derivatograms of samarium and dysprosium 2,4-dinitrobenzoates. 2,4-Dinitrobenzoates of rare earth elements are dehydrated in one step. The dehydration process connected with the endothermic effect proceeds in the temperature ranges 319–421 K for light lanthanides and La and 427–505 K for heavy ones and Y. In the series of light lanthanide 2,4-dinitrobenzoates, the least thermally stable complex is the hydrate of cerium which starts to lose the crystallization water at 319 K while the most thermally stable are lanthanum and samarium 2,4-dinitrobenzoates that

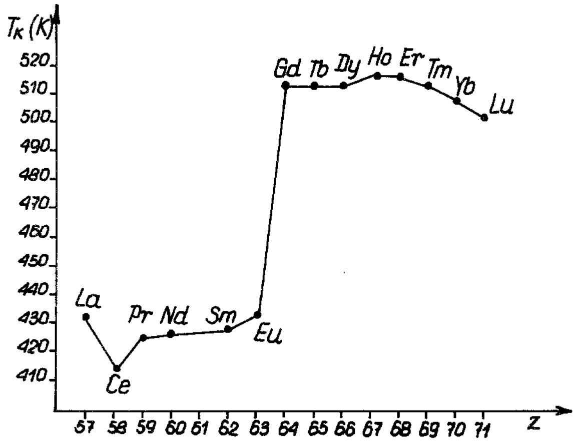

Fig. 3. Relationship between anhydrous salt formation and Z

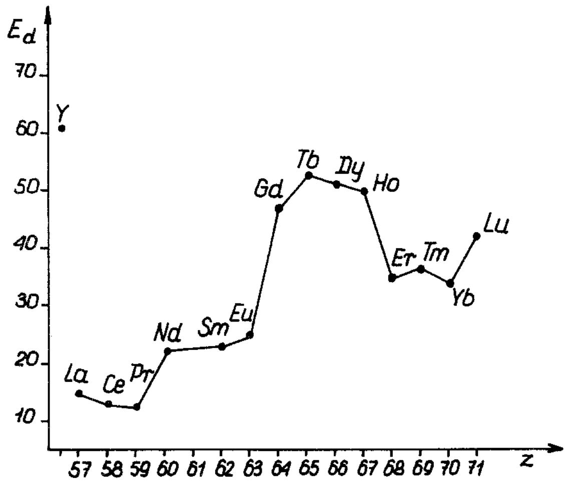

Fig. 4. Relationship between activation energy of dehydration reaction and Z

release crystallization water molecules at 355 K. For the heavy lanthanide 2,4-dinitrobenzoates, the complex of lutetium which expels the crystallization water at 427 K is the least thermally stable. Being the most thermally stable, the dihydrate of erbium 2,4-dinitrobenzoate starts to dehydrate at 462 K. In the temperature range from 413 K (for Ce) and 515 K (for Ho and Er) the anhydrous salts of rare earth 2,4-dinitrobenzoates are formed The values of the initial temperature of dehydration process and the temperature of the anhydrous complex formation do not regularly change with the atomic number of element (Fig. 3). The values of the initial temperature of the dehydration process are greater for heavy lanthanide 2,4-dinitrobenzoates than for the light ones. It is possible to suppose that water molecules, being lost in one step are bound in these complexes in various ways. Being lost at lower temperatures it is probably outer sphere water, while the inner one is lost at higher temperatures. From TG and DTA curves the activation energy of dehydration reaction for dihydrates of 2,4-dinitrobenzoates were calculated by means of the Fateev and Plentnew method [10] (Table 3, Fig. 4). The greater values of the activation energy for complexes of heavy lanthanides compared to the light ones indicate that the water molecules are not bound equally in these complexes. Yttrium 2,4-dinitrobenzoate has the highest value of activation energy while cerium and praseodymium the smallest one. The solubilities of 2,4-dinitrobenzoates of Y, La and lanthanides measured in water at 298 K (Table 3), being in the order of 10^{-2} mol dm^{-3}, are in good agreement with those determined for rare earth element 2-nitrobenzoates [11] but higher than for 4-nitrobenzoates of those elements [12].

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