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Preparation and Properties of Rare Earth 4-Nitrophthalates

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Rare earth (Y, La–Lu) 4-nitrophthalates were prepared and studied using IR spectroscopy, TG, DTG and DTA. Their compositions were determined as well as their solubilities in water at 295 K. The rare earth complexes were obtained as solids with a 2:3 ratio of metal to organic ligand. 4-Nitrophthalates of Y, La–Eu, Dy–Tm were crystalline solids, whereas those of Gd, Tb, Yb and Lu were amorphous. The COO^- group in the prepared complexes acts as bidentate chelating. The complexes are stable at room temperature. During heating they are dehydrated in one (Y, La, Pr–Yb), two (Ce, Lu) or three (La) steps, and then the anhydrous complexes decompose explosively.

INTRODUCTION

4-Nitrobenzene-1,2-dicarboxylic acid $NO_2C_6H_3(COOH)_2$, known as 4-nitrophthalic acid, is a yellow crystalline solid soluble in water (especially in hot water) and ethanol and insoluble in benzene, chloroform, CCl_4 and CS_2.[1,2] The salts of 4-nitrophthalic acid are little known. 4-Nitrophthalates of K, Ag (I) and Ba (II) have been isolated in solid state and some of their properties were studied.[1] Complexes of rare earth elements with 4-nitrophthalic acid in solid state have not been prepared and studied so far.

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Nikolski *et al.*[3] have determined the stability constant for the europium (III) complex $[Eu(C_8H_3NO_6)]^+$ by the ion exchange method.

The aim of the present work was to prepare 4-nitrophthalates of rare earths (Y, La-Lu, without Pm) as solids under the same conditions and to examine some of their physical and chemical properties.

EXPERIMENTAL

Reagents

4-Nitrophthalic acid (Merck-Schuchard), Ln_2O_3 (Ln = Y, La, Nd, Sm, Gd), $Ce(NO_3)_3 \cdot 6H_2O$ and Pr_6O_{11} – 99.9%, (prepared in our laboratory), Eu_2O_3 and Tb_4O_7 – 99.9% (Koch Light Laboratories Ltd., England), Dy_2O_3 and Tm_2O_3 – 99% (Riedel-de Han), Ho_2O_3 and Lu_2O_3 – 99.9% (POCh Gliwice), Er_2O_3 – 99.9% (Aldrich Chem. Co), Yb_2O_3 – 99.9% (Fluka AG), HCl p.a. and NH_3 aq *p.a.* (POCh Gliwice) were used.

Preparation

4-Nitrophthalates of Y (III) and lanthanides (III) from La to Ho were prepared by dissolving freshly precipited lanthanide hydroxides (Ce (III) was used as carbonate) in a hot 0.1 M solution of 4-nitrophthalic acid (pH 4.3–4.5) and mixed in mother liquor for 10 h. ($Ln(OH)_3$ was precipitated by adding ammonia to a hot $LnCl_3$ solution, filtered off and washed with water to remove NH_4^+ ions).

The precipitates formed were filtered off, washed with water and dried at 303 K to constant mass.

4-Nitrophthalates of Er (III), Tm (III), Yb (III) and Lu (III) were prepared by dissolving $Ln(OH)_3$ in a hot 0.1 M solution of 4-nitrophthalic acid and subsequent crystallization at room temperature. The solids formed were filtered off, washed with hot water and dried at 303 K to a constant weight. The yields of lanthanide 4-nitrophthalates were about 70–90%.

Elemental Analysis

The contents of carbon, hydrogen and nitrogen in the prepared complexes were determined by elemental analysis using a CHN2400 Perkin Elmer analyser. The content of rare earth elements was determined by the gravimetric method by transforming the complexes into oxides *via* oxalates. The content of crystallization water was determined from the TG curves and by heating the prepared complexes at 523 K.

IR Spectra

The IR spectra of 4-nitrophthalic acid, its rare earth complexes and sodium salt were recorded over the range 4000–400 cm^{-1} using a SPECORD M–80 spectrophotometer. Samples were prepared as KBr discs.

Thermal Analysis

The thermal stability of the prepared 4-nitrophthalates was determined using Q–1500 D derivatograph at a heating range of 2.5 deg · min^{-1}. Samples (200 mg) were heated in air in platinum crucibles to 523 K with the sensitivity TG – 50 mg, sensitivity of DTG and DTA was regulated by MOM Derill computer program. Al_2O_3 was used as a standard.

Determination of Solubility

Solubility of the prepared complexes in water was measured at 295 K. Saturated solutions were prepared under isothermal conditions. The content of Ln(III) ions (from La to Ho) was determined by the oxalate method. The content of Er(III), Tm(III), Yb(III) and Lu(III) ions was determined by the spectrophotometric method with arsenazo III.

RESULTS AND DISCUSSION

4-Nitrophthalates of rare earth elements (Y, La–Lu) were prepared as solids of the color characteristic of lanthanide (III) ions and as complexes with a 2:3 molar ratio of metal to organic ligand, with a general formula: $Ln_2[NO_2C_6H_3(COO)_2]_3 \cdot nH_2O$, where n = 5 for La(III), Pr–Gd(III) and D(III); n = 6 for Y(III), Ce(III), Tb(III) and Ho–Tm(III); n = 8 for Yb–Lu(III) (Table I). The hydration degree of the complexes does not change regularly with decreasing the ionic radius in the lanthanide series.

In order to confirm the composition of the prepared complexes and to determine the metal-ligand coordination manner, the IR spectra of 4-nitrophthalic acid and of the prepared lanthanide and sodium 4-nitrophthalates were recorded (Table II).

The IR spectra of 4-nitrophthalic acid exhibit the following absorption bands: the broad absorption band of the OH group with the maximum at 3112 cm^{-1}, the strong band of C = O in the COOH group at 1732 cm^{-1}, the band of the stretching vibration of C–O in C–OH group at 1308 cm^{-1}, the band of deformation vibration of the OH group in the ring plane at 1408 cm^{-1}, absorption bands of the asymmetrical ($\nu_{as}NO_2$) and symmetrical (ν_sNO_2) vibrations of the NO_2 group at 1536 and 1352 cm^{-1}, respectively, the band of C–N at 1236 cm^{-1}, the bands of the stretching vibrations of C–C at 1608, 1496, 1472 cm^{-1}, the bands of the C–H group in the benzene ring trisubstituted in the 1,2,4-position at 1144, 1120, 1064, 912, 864, 808 cm^{-1} and the bands of deformation vibrations of the C–H at 740, 692, 656 and 588 cm^{-1}.

The IR spectra of all 4-nitrophthalates are quite similar. Conversion of the acid to the salt is paralleled by a change in IR spectra. The broad band

TABLE I

Analytical data of the rare earth 4-nitrophthalates

Complex	% C		% H		% N		% M	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$Y_2L_3 \cdot 6H_2O$	31.56	32.0	2.32	2.2	4.60	4.0	19.47	19.4
$La_2L_3 \cdot 5H_2O$	28.96	28.6	1.92	1.9	4.22	4.0	27.91	27.4
$Ce_2L_3 \cdot 6H_2O$	28.38	28.6	2.08	1.9	4.13	4.0	27.59	27.5
$Pr_2L_3 \cdot 5H_2O$	28.85	28.7	1.92	1.9	4.20	3.8	28.20	28.7
$Nd_2L_3 \cdot 5H_2O$	28.65	28.4	1.90	1.9	4.17	3.9	28.68	28.7
$Sm_2L_3 \cdot 5H_2O$	28.31	28.3	1.88	1.9	4.12	3.8	29.53	29.2
$Eu_2L_3 \cdot 5H_2O$	28.22	28.2	1.87	1.8	4.11	3.8	29.75	29.7
$Gd_2L_3 \cdot 5H_2O$	27.93	27.9	1.86	1.8	4.07	3.7	30.48	30.9
$Tb_2L_3 \cdot 6H_2O$	27.37	27.8	2.01	1.9	3.99	3.4	30.17	30.1
$Dy_2L_3 \cdot 5H_2O$	27.65	27.6	1.84	1.8	4.03	3.4	31.18	31.2
$Ho_2L_3 \cdot 6H_2O$	27.06	27.4	1.99	1.9	3.94	3.3	30.96	30.9
$Er_2L_3 \cdot 6H_2O$	26.94	27.0	1.98	1.9	3.93	3.3	31.26	31.1
$Tm_2L_3 \cdot 6H_2O$	26.86	26.9	1.97	1.9	3.91	3.6	31.48	31.5
$Yb_2L_3 \cdot 8H_2O$	25.79	26.0	2.25	2.2	3.76	3.3	30.97	30.7
$Lu_2L_3 \cdot 8H_2O$	25.70	25.1	2.24	2.2	3.74	3.0	31.02	31.0

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of valency vibration of the OH group in H_2O is shifted to higher frequencies, as compared to that band for free acid and appears at 3432–3376 cm^{-1}. The spectra of these complexes do not show absorption bands characteristic of COOH group, but exhibit strong absorption bands of the asymmetrical and symmetrical valency vibrations of the COO^- group at 1568–1550 cm^{-1} and 1436–1412 cm^{-1}, respectively, and the absorption bands of the Ln–O bond at 528–504 cm^{-1} (Table II).

The frequency of the absorption band of the metal-oxygen bond decreases insignificantly with decreasing the ionic radius in the lanthanide series, which indicates that the complex stability changes gradually.[4]

The small values of the displacements of the position of the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ bands found for lanthanide 4-nitrophthalates (or their lack), as compared to those bands observed for 4-nitrophthalic acid (Table II), suggest that the NO_2 group takes no part in metal-ligand coordination.[5]

The positions of the absorption bands of the aromatic ring vibrations in the IR spectra of complexes within the range 1608–1472 cm^{-1} are only slightly shifted in comparison with the spectra of the 4-nitrophthalic acid. It

TABLE II

Frequency of the absorption bands of asymmetrical and symmetrical vibrations of the COO^- and NO_2 groups and metal-oxygen bond in lanthanide 4-nitrophthalates (cm^{-1})

Complex	$\nu_{as}(COO)$	$\nu_s(COO)$	$\Delta\nu$	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	$\nu(M–O)$
$Y_2L_3 \cdot 6H_2O$	1556	1436	120	1525	1352	516
$La_2L_3 \cdot 5H_2O$	1564	1436	128	1524	1352	528
$Ce_2L_3 \cdot 6H_2O$	1556	1436	120	1526	1352	528
$Pr_2L_3 \cdot 5H_2O$	1550	1432	118	1536	1356	516
$Nd_2L_3 \cdot 5H_2O$	1550	1432	118	1536	1356	512
$Sm_2L_3 \cdot 5H_2O$	1550	1436	114	1536	1356	516
$Eu_2L_3 \cdot 5H_2O$	1550	1436	114	1536	1352	512
$Gd_2L_3 \cdot 5H_2O$	1552	1436	116	1536	1352	512
$Tb_2L_3 \cdot 6H_2O$	1554	1436	118	1535	1352	512
$Dy_2L_3 \cdot 5H_2O$	1554	1436	118	1535	1352	512
$Ho_2L_3 \cdot 6H_2O$	1554	1436	118	1536	1352	512
$Er_2L_3 \cdot 6H_2O$	1554	1436	118	1536	1352	504
$Tm_2L_3 \cdot 6H_2O$	1556	1436	120	1524	1352	504
$Yb_2L_3 \cdot 8H_2O$	1560	1424	136	1534	1348	504
$Lu_2L_3 \cdot 8H_2O$	1568	1418	150	1535	1348	504
Na_2L	1568	1412	156	1528	1344	

$\Delta\nu = \nu_{as}(COO)–\nu_s(COO)$

has been found that the lanthanide ions only slightly influence the change of electron density in the aromatic ring.[6]

The magnitudes of separation ($\Delta\nu$) between frequencies due to asymmetrical and symmetrical vibrations of the COO^- group for Y(III) and lanthanide (III) 4-nitrophthalates (except for 4-nitrophthalates of Yb(III) and specialy of Lu(III)) (Table II) are just the same or slightly different (which suggests that the participation of the ionic bond is similar) and are far smaller than that found for the sodium salt, which indicates a smaller degree of ionic bond in these complexes, as compared to the sodium salt. The participation of the ionic bond in 4-nitrophthalate of Yb(III) and, particularly, in 4-nitrophthalate of Lu(III) is much higher than that in the remaining complexes.

The bands of asymmetrical vibrations $\nu_{as}COO^-$ of the lanthanide complexes with 4-nitrophthalic acid are shifted to lower frequencies and the bands of symmetrical vibrations ν_s COO^- to higher ones compared with the

TABLE III

Thermal data of dehydration of lanthanide 4-nitrophthalates, and their solubilities in water at 295 K

Complex	Temperature range of dehydration [K]	Loss of weight %		Loss of H_2O molecules [n]	Temperature of endo effect [K]	Solubility [(mol dm^{-3} × 10^{-3})]
		calculated	found			
$Y_2L_3 \cdot 6H_2O$	299–510	11.83	11.8	6	418	1.71
$La_2L_3 \cdot 5H_2O$	301–500	9.05	9.0	5	343,409,464	1.06
$Ce_2L_3 \cdot 6H_2O$	300–496	10.64	10.7	6	350,457	0.92
$Pr_2L_3 \cdot 5H_2O$	302–504	9.01	8.9	5	440	0.48
$Nd_2L_3 \cdot 5H_2O$	300–484	8.95	8.9	5	440	0.52
$Sm_2L_3 \cdot 5H_2O$	302–459	8.85	9.0	5	433	0.48
$Eu_2L_3 \cdot 5H_2O$	300–460	8.82	9.1	5	439	0.60
$Gd_2L_3 \cdot 5H_2O$	308–460	8.73	8.7	5	433	0.92
$Tb_2L_3 \cdot 6H_2O$	300–507	10.26	10.2	6	416	0.89
$Dy_2L_3 \cdot 5H_2O$	300–444	8.64	8.7	5	418	0.92
$Ho_2L_3 \cdot 6H_2O$	307–498	10.15	9.8	6	419	1.33
$Er_2L_3 \cdot 6H_2O$	307–498	10.10	9.8	6	417	2.00
$Tm_2L_3 \cdot 6H_2O$	309–478	10.07	10.0	6	413	3.91
$Yb_2L_3 \cdot 8H_2O$	302–454	12.89	13.0	8	365	36.41
$Lu_2L_3 \cdot 8H_2O$	304–468	12.85	12.9	8	362,393	106.30

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absorption bands of the sodium salt (only the frequency of asymmetrical vibration band $\nu_{as}COO^-$ for Lu(III) and Na is the same).

The splitting $\Delta\nu$ and the frequency shift of the ν_{as} (COO) and ν_s (COO) for the studied complexes, compared to the sodium salt, suggest, according to the spectroscopic criterion,[7,8] that the carboxylate group is probably bidentate chelating. This suggestion could be confirmed by the crystal and molecular structure of monocrystals but they have not been prepared so far.

4-Nitrophthalates of Y(III) and lanthanides *decompose explosively* during heating,(similarly to other compounds with nitrogroups) and that is why their thermal stability was studied within the temperature range of 293–523 K (Table III). The hydrated 4-nitrophthalates of rare earth elements are stable up to 299–309 K and are dehydrated within the temperature range of 299–510 K, being converted to anhydrous complexes. The loss of the crystallization water molecules is associated with a strong endothermic effect at 343–464 K (Figure 1). The low temperature of dehydration sug-

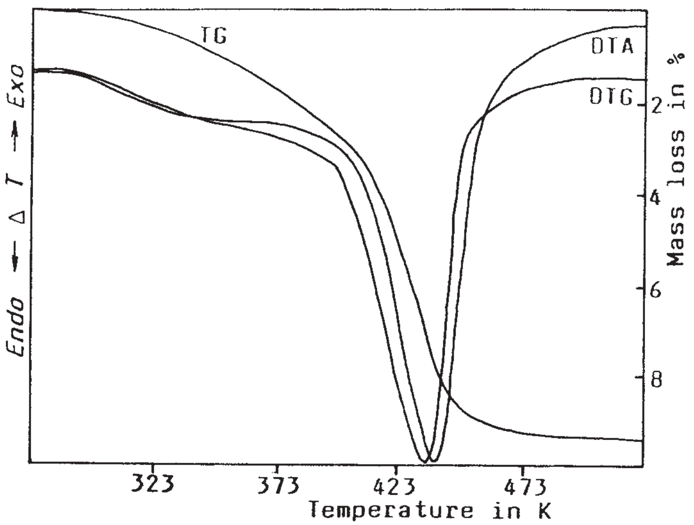

Figure 1. TG, DTG and DTA curves of $Eu_2(C_8H_3NO_6)_3 \cdot 5H_2O$.

gests (like for other similar crystallohydrates of Ln [9–14]) that the crystallization water in the complexes studied is probably lattice water. Dehydration of the Ce(III) (Figure 2) and Lu(III) complexes is accompanied by two endothermic effects whereas that of the La(III) 4-nitrophthalate (Figure 3) by three. This fact suggests that the crystallization water molecules in these compounds are bonded in some other way than in the remaining complexes.

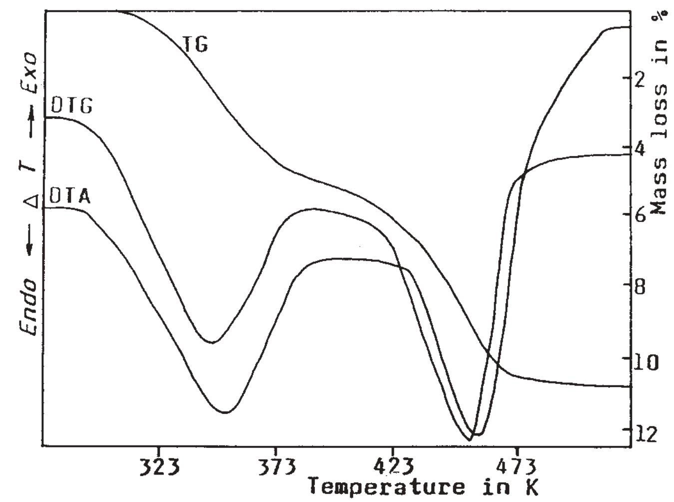

Figure 2. TG, DTG and DTA curves of $Ce_2(C_8H_3NO_6)_3 \cdot 6H_2O$.

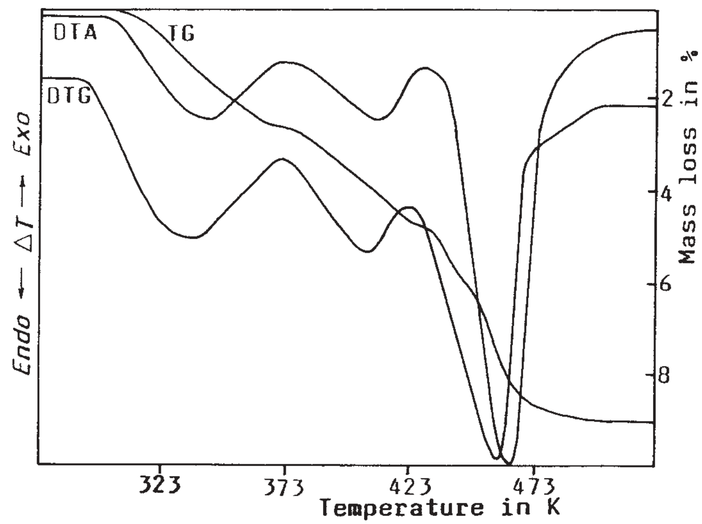

Figure 3. TG, DTG and DTA curves of $La_2(C_8H_3NO_6)_3 \cdot 5H_2O$.

Solubilities of Y(III) and lanthanide 4-nitrophthalates in water at 295 K Figure 3. TG, DTG and DTA curves of $La_2(C_8H_3NO_6)_3 \cdot 5H_2O$ were determined (Table III). They are of the order of 10^{-3}–10^{-4} $mol \cdot dm^{-3}$ and change irregularly in the lanthanide series. Solubilities of light lanthanide 4-nitrophthalates decrease with the increasing atomic number of lanthanide, whereas the solubilities of heavy lanthanide 4-nitrophthalates increase with the increasing atomic number of lanthanide (Figure 4). Ytterbium and luttetium 4-nitrophthalates are much more soluble than the remaining complexes, which confirmes their different structure. The solubility of the prepared complexes changes with the increasing atomic number of lanthanide (Figure 4) according to the double–double effect.[15] 4-Nitrophthalates of Y(III) and lanthanides are less soluble in water than the corresponding phthalates (10^{-3}mol · dm^{-3})[16] and the 3-nitrophthalates (10^{-2}–10^{-3} mol dm^{-3}).[17]

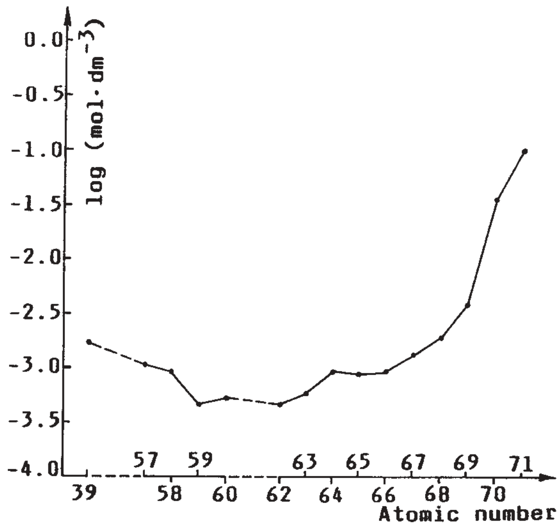

Figure 4. Solubility of Y (III) and lanthanide 4-nitrophthalates in water at 295 K.

On the basis of the obtained results, it is possible to conclude that the position of NO_2 group in benzene ring influences the electron cloud density on the carbon atom of the COO^- group and causes a change in the structure and properties of rare earth 4-nitrophthalates, as compared to those of the corresponding 3-nitrophthalates.[17,18]

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SAŽETAK

Sinteza i svojstva 4-nitroftalata rijetkih zemalja

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Pripravljeni su 4-nitroftalati rijetkih zemalja (Y, La-Lu), određen im je sastav i topljivost u vodi pri 295 K. Snimljeni su IR spektri i rentgenogrami praha dobivenih kompleksa. Kompleksi rijetkih zemalja dobiveni su kao krutine s omjerom metal:organski ligand = 2:3. Kristalni su 4-nitroftalati Y, La-Eu i Dy-Tm dok su 4-nitroftalati Gd, Tb, Yb i Lu amorfni. U priređenim kompleksima skupina COO^- djeluje bidentatno. Kompleksi su stabilni na sobnoj temperaturi, zagrijavanjem se dehidriraju u jedan (Y, La, PrYb), dva (Ce,Lu) ili tri (La) stupnja, nakon čega se eksplozivno raspadaju.