Monatshefte für Chemie 120, 1075–1083 (1989)

Monatshefte für Chemie
Chemical Monthly

Preparation and Properties of Yttrium, Lanthanum, and Lanthanide 3,5-Dinitrobenzoates

Wiesława Ferenc

Department of Inorganic and General Chemistry, Institute of Chemistry,
Marie Curie-Skłodowska University, PL-20-031 Lublin, Poland

Summary. The condition of the formation of rare earth 3,5-dinitrobenzoates were studied and their quantitative composition and solubilities in water at 298 K determined (their solubilities are of the order of 10^{-4} mol dm^{-3}). From the values of solubilities in water the solubility products were established (in the order of 10^{-12} mol^{4}dm^{-12}). The IR and X-ray spectra for the hydrated and dehydrated complexes were recorded and studied. All complexes are crystalline compounds. The condition of thermal decomposition of the complexes was also investigated. On heating above 573 K the 3,5-dinitrobenzoates decompose explosively and undergo a melting process at the same time. Accordingly, the thermal decomposition for the complexes was studied in the temperature range 273–573 K. The thermal stability data reveal them to dehydrate in two steps. From the obtained results it appears that during the dehydration process no izomerization of the nitro group to the nitrito group occurs.

Keywords. Yttrium; Lanthanum and lanthanide 3,5-dinitrobenzoates; Complexes of rare earth elements with 3,5-dinitrobenzoic acid.

Herstellung und Eignenschaften von Y-, La- und Lanthaniden-3,5-Dinitrobenzoaten

Zusammenfassung. Die Bedingungen zur Darstellung von Y-, La- und Lanthaniden-3,5-Dinitrobenzoaten wurden untersucht. Ihre quantitative Zusammensetzung und ihre Wasserlöslichkeit bei 298 K wurden bestimmt (die Löslichkeit ist in der Größenordnung 10^{-4} mol dm^{-3}). Die Infrarot- und Röntgenspektren der erhaltenen Komplexe sowie der 3,5-Dinitrobenzoate der seltenen Erden nach der Dehydratisierung wurden gemessen. Es wurde festgestellt, daß es sich stets 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 3,5-Dinitrobenzoate der seltenen Erden wurde im Temperaturbereich von 273–523 K untersucht. Es wurde festgestellt, daß die Y-, La-, und Lanthaniden – 3,5-Dinitrobenzoate bei Temperaturerhöhung oder im Dehydratisierungsprozeß keine Umgruppierung in die entsprechenden Nitritoverbindungen erleiden.

Introduction

3,5-Dinitrobenzoic acid is a white, crystalline solid, sparingly soluble in water [1]. Its electrolytic dissociation constant is equal to $1.63 \cdot 10^{-3}$ ($t = 25$°C). The compounds of 3,5-dinitrobenzoic acid are comparatively little known. A literature survey reveals that its salts with the following cations: Na^+ [1, 2], NH_4^+ [1, 3],

K^+ [1, 2, 4, 5], Ag^+ [1, 6, 7], Cu^{2+} [8], Pb^{2+} [1, 3], Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+} [1], Ni^{2+} [9] and Hg^{2+} [10] have been prepared.

The object of the present study was to obtain in solid state the 3,5-dinitrobenzoates of Y, La, and lanthanides with a metal to ligand ratio of 1 : 3 and to examine some of their properties.

Experimental

3,5-Dinitrobenzoates of yttrium, lanthanum and lanthanides were prepared by the addition of the equivalent quantities of 0.2 *M* ammonium 3,5-dinitrobenzoate (*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 for removing 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 constant of crystallization water molecules were determined from the curve of TG and by isothermal heating of the complexes at 573 K. The IR spectra for the complexes, the spectra for 3,5-dinitrobenzoic acid, sodium 3,5-dinitrobenzoate and the dehydrated 3,5-dinitrobenzoates of yttrium, lanthanum, and lanthanides and for sodium nitrite were recorded as KBr discs on an UR-20 spectrophotometer (range 4 000–400 cm^{-1}). Some of the experimental data are collected in Table 2. The X-ray diffraction patterns of hydrated and dehydrated rare earth element 3,5-dinitrobenzoates and lanthanide oxides obtained from the ignition of the oxalates and 3,5-dinitrobenzoates of Y, La, and lanthanides were taken on a DRON-2 diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\theta = 4 - 80°$ 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 θ-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).

Table 1. Analytical data

Complex $L = C_7H_3N_2O_6$	% C		% N		% H		% M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$YL_3 \cdot 3\,H_2O$	32.47	32.77	10.82	10.80	1.93	1.88	11.45	11.56
$LaL_3 \cdot 3\,H_2O$	30.51	30.18	10.17	10.14	1.81	1.92	16.81	16.68
$CeL_3 \cdot 3\,H_2O$	30.46	30.60	10.15	10.18	1.81	1.80	16.92	16.89
$PrL_3 \cdot 3\,H_2O$	30.46	30.55	10.15	10.30	1.81	1.90	17.01	17.20
$NdL_3 \cdot 3\,H_2O$	32.19	32.29	10.73	10.74	1.91	2.00	18.42	18.36
$SmL_3 \cdot 3\,H_2O$	30.09	30.29	10.03	10.05	1.79	1.80	17.95	18.03
$EuL_3 \cdot 3\,H_2O$	30.03	30.06	10.01	10.26	1.78	1.82	18.11	18.22
$GdL_3 \cdot 3\,H_2O$	29.84	29.86	9.94	9.91	1.77	1.70	18.62	18.57
$TbL_3 \cdot 3\,H_2O$	29.79	29.74	9.93	9.99	1.77	1.83	18.78	18.68
$DyL_3 \cdot 3\,H_2O$	29.66	29.68	9.88	9.66	1.76	1.80	19.12	19.22
$HoL_3 \cdot 3\,H_2O$	29.60	29.90	9.86	9.92	1.76	1.68	19.37	19.54
$ErL_3 \cdot 3\,H_2O$	29.49	29.44	9.86	9.94	1.75	1.72	19.57	19.58
$TmL_3 \cdot 3\,H_2O$	29.42	29.50	9.80	9.82	1.75	1.82	19.77	19.64
$YbL_3 \cdot 3\,H_2O$	29.30	29.38	9.76	9.68	1.74	1.68	20.11	20.01
$LuL_3 \cdot 3\,H_2O$	29.23	29.18	9.74	9.80	1.74	1.72	20.29	20.19

The solubilities of 3,5-dinitrobenzoates of yttrium, lanthanum, and lanthanides in water at 298 K were determined by measuring the concentration of Lu^{3+} ions in saturated solutions by the oxalate method (Table 3).

Results and Discussion

3,5-Dinitrobenzoates of yttrium, lanthanum, and lanthanides were obtained in crystalline form with the colour characteristic for Ln^{3+} ions and a metal to ligand ratio of 1 : 3 and the general formula $Ln\ (C_7H_3O_6N_2) \cdot 3\,H_2O$ where Ln = Y, La, Ce – Lu. The compounds were characterized by elemental analyses (Table 1) and IR spectra. All rare earth 3,5-dinitrobenzoates show similar solid-state IR spectra. However the characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salts. The band of the COOH group at 1 710 cm^{-1}, present in the acid spectrum, completely disappears in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of the COO^- group occur at 1 615–1 610 cm^{-1} and 1 430–1 400 cm^{-1} respectively. The bands with the maxima at 3 480–3 450 cm^{-1} confirm the presence of crystallization water molecules and the bands at 1 555–1 545 cm^{-1} and 1 345 cm^{-1} the asymmetric and symmetric vibrations of NO_2 groups, respectively. The stretching vibrations of the benzene ring, γ(C-C) occur at 1 575 cm^{-1} and 1 470 cm^{-1} while those of the C-H groups at 3 095 cm^{-1}. The out-of-plane deformation vibration bands of C-H groups, γ(C-H) are observed at 920 cm^{-1}, 795 cm^{-1} and 725 cm^{-1} whereas those in plane, β(C-H), at 1 080 cm^{-1}. The bands due to metal-oxygen bond appear at 485–450 cm^{-1}. Their shift changes from La to Lu to higher frequencies are probably

Table 2. Frequencies of absorption bands of $-COO^-$ and $-NO_2$ for Na, Y, La, and lanthanide 3,5-dinitrobenzoates and 3,5-dinitrobenzoic acid (cm^{-1})

Compound $L = C_7H_3N_2O_6$	$\gamma_{as}OCO$	$\gamma_{sym}OCO$	$\Delta\gamma$	$\gamma_{as}\ (NO_2)$	$\gamma^a_{sym}\ (NO_2)$	$\Delta\gamma_{(NO_2)}$	γ_{M-O}
$YL_3 \cdot 3\,H_2O$	1 610	1 420	190	1 555	1 345	210	450
$LaL_3 \cdot 3\,H_2O$	1 610	1 400	210	1 555	1 345	210	450
$CeL_3 \cdot 3\,H_2O$	1 610	1 400	210	1 555	1 345	210	450
$PrL_3 \cdot 3\,H_2O$	1 610	1 400	210	1 555	1 345	210	450
$NdL_3 \cdot 3\,H_2O$	1 610	1 405	205	1 550	1 345	205	450
$SmL_3 \cdot 3\,H_2O$	1 610	1 405	205	1 550	1 345	205	450
$EuL_3 \cdot 3\,H_2O$	1 610	1 405	205	1 550	1 345	205	450
$GdL_3 \cdot 3\,H_2O$	1 610	1 410	200	1 550	1 345	205	450
$TbL_3 \cdot 3\,H_2O$	1 610	1 415	195	1 555	1 345	210	455
$DyL_3 \cdot 3\,H_2O$	1 615	1 420	195	1 550	1 345	205	460
$HoL_3 \cdot 3\,H_2O$	1 615	1 425	190	1 550	1 345	205	465
$ErL_3 \cdot 3\,H_2O$	1 615	1 425	190	1 555	1 345	210	470
$TmL_3 \cdot 3\,H_2O$	1 615	1 425	190	1 550	1 345	205	475
$YbL_3 \cdot 3\,H_2O$	1 615	1 430	185	1 540	1 345	195	480
$LuL_3 \cdot 3\,H_2O$	1 615	1 430	185	1 545	1 345	200	485
NaL	1 620	1 395	225	1 550	1 350	200	–
HL	–	–	–	1 550	1 350	200	–

[a] For all 3,5-dinitrobenzoates of Y, La, and lanthanides the bands of $\gamma_{sym}\ (NO_2)$ are splitted

caused by increasing stability of the *M*-O bond with increasing atomic numbers and ionic potentials of the elements (Table 2). The magnitudes of separation, $\Delta\gamma$, between the frequencies due to γ_{asym} OCO and γ_{sym} OCO in these complexes are lower than in the sodium salt which indicates a smaller degree of ionic bond in these complexes compared to that of sodium (Table 2). The close values of $\Delta\gamma$ may indicate the similar way of lanthanide ion coordinations with benzenedinitrocarboxylate ligands, but they decrease with decreasing ionic radii of elements (which probably leads to the decrease of the OCO angle of carboxylate group [11]), and with increasing bond covalency in the heavy lanthanides.

From the values of $\Delta\gamma$ it is not possible to define the degree of the covalent bond on account of the changes of the OCO bond angle with ionic radii in the lanthanide ions [11]. The directions of shifts in the frequencies due to γ_{asym} OCO and γ_{sym} OCO are lower (or remain unaltered) and higher, respectivley, relative to those in sodium 3,5-dinitrobenzoate. Therefore, the carboxylate ion is supposed to be a bidentate, chelating ligand [12] but probably with incomplete equalization of its bond lengths. Being higher for heavy lanthanide 3,5-dinitrobenzoates than for light ones the frequencies due to γ_{asym} OCO and γ_{sym} OCO may indicate a small change in the carboxylate group structure. Probably its greater symmetrization connected with an increase in covalency of bonds appears.

The small values of the displacements in the position of γ_{asym} (NO_2) and γ_{sym} (NO_2) bands for 3,5-dinitrobenzoates of rare earth elements (or their lack) relative to those in 3,5-dinitrobenzoic acid (Table 2) are indicative of the only weak interaction of NO_2 groups with lanthanide ions, which practically leads to the lack of their coordination to metal ions.

The small splittings of γ_{sym} (NO_2) bands probably result from the interaction of the ligands and water molecules in the complexes and their polar properties. The spectra of the heavy lanthanide complexes characterized by relatively more intense aromatic bands, (compared with light lanthanides) are closer to the spectrum of 3,5-dinitrobenzoic acid. This, being connected with an increase in covalency and the degree of delocalization of band in the heavy lanthanides, leads probably to an increase of the delocalization of π electrons and the intensity of the aromatic bands of γ(C$\cdots$C) of the benzene ring. The spectra for hydrated and dehydrated complexes and for sodium nitrite reveal that the 3,5-dinitrobenzoates of rare earth elements, which are isolated in solid form, are nitro complexes and no isomerization of the nitro group to nitrito takes place with rising temperature [13–16]. The lack of splittings of γ_{sym} (NO_2) bands in the spectra of the dehydrated complexes relative to the hydrated ones may suggest that crystallization water molecules probably cause the changes in the structure of the ligand interactions.

More intense aromatic bands in the hydrated 3,5-dinitrobenzoates compared to dehydrated ones may indicate that in the hydrates the water molecules decrease the metal-ligand interaction causing the decrease of the deformation of the electron cloud in the ring and the increase of the intensity of aromatic bands in the trihydrates. From the diffractogram analysis the dehydrated and hydrated 3,5-dinitrobenzoates of rare earth elements were found to be crystalline compounds characterized by low symmetry, the large size of unit cells, different structures and different degrees of crystallization. 3,5-Dinitrobenzoates of heavy lanthanides are isostructural. The anhydrous 3,5-dinitrobenzoates appear to have a less degree of crystallinity than the hydrated ones. No changes of their structures compared to

Table 3. Temperature ranges of the dehydration process, activation energies of dehydration reactions, solubility in water (293 K), and solubility products of 3,5-dinitrobenzoates of Y, La, and lanthanides

Complex $L = C_7H_3N_2O_6$	ΔT_1^a (K)	Loss of weight		n^d	ΔT_2^a (K)	Loss of weight		n^d	T_{max}^b (K)		T_k^c (K)	E (kJ mol^{-1})		Solubility as anhydrous salt $\times 10^{-4}$mol dm^{-3}	Solubility products (J) $\times 10^{-12}$mol^4 dm^{-12}	$pI = -\log I$
		Calcd (%)	Found (%)			Calcd (%)	Found (%)					E_1	E_2			
$YL_3 \cdot 3H_2O$	309–371	4.63	4.80	2	422–471	6.95	7.05	1	368	459	482	35	16	11.7	50.4	10.30
$LaL_3 \cdot 3H_2O$	385–431	4.35	4.35	2	433–483	6.53	6.58	1	419	467	487	52	39	12.8	70.2	10.15
$CeL_3 \cdot 3H_2O$	314–422	4.35	4.25	2	439–481	6.52	6.42	1	410	467	487	37	22	7.4	8.2	11.09
$PrL_3 \cdot 3H_2O$	303–428	4.35	4.30	2	447–486	6.52	6.62	1	408	473	490	45	22	7.0	6.6	11.18
$NdL_3 \cdot 3H_2O$	305–403	4.59	4.79	2	415–491	6.89	6.98	1	390	479	501	24	20	7.4	7.9	11.10
$SmL_3 \cdot 3H_2O$	305–395	4.29	4.18	2	436–488	6.44	6.54	1	380	470	491	21	17	6.4	4.6	11.34
$EuL_3 \cdot 3H_2O$	310–393	4.29	4.30	2	429–482	6.43	6.50	1	378	468	489	27	15	8.2	12.0	10.17
$GdL_3 \cdot 3H_2O$	303–391	4.26	4.28	2	429–480	6.39	6.29	1	375	466	493	16	15	5.9	3.4	11.47
$TbL_3 \cdot 3H_2O$	310–390	4.25	4.25	2	426–478	6.38	6.50	1	374	465	482	40	16	8.3	13.0	10.89
$DyL_3 \cdot 3H_2O$	308–390	4.23	4.25	2	419–473	6.35	6.37	1	372	460	481	58	17	7.9	10.6	10.97
$HoL_3 \cdot 3H_2O$	305–387	4.22	4.25	2	424–477	6.34	6.37	1	371	461	485	32	16	9.7	24.2	10.61
$ErL_3 \cdot 3H_2O$	309–383	4.21	4.22	2	415–475	6.32	6.42	1	364	453	482	43	13	9.6	2.1	11.67
$TmL_3 \cdot 3H_2O$	303–380	4.20	4.20	2	409–462	6.30	6.32	1	359	444	463	84	12	10.7	36.0	10.44
$YbL_3 \cdot 3H_2O$	315–377	4.18	4.18	2	402–460	6.27	6.25	1	353	434	463	48	10	13.6	92.3	10.03
$LuL_3 \cdot 3H_2O$	303–373	4.17	4.17	2	392–444	6.26	6.25	1	350	425	452	29	23	16.2	185.0	9.73

[a] ΔT_1, ΔT_2: temperature ranges corresponding to the endothermic loss of molecules of crystallization water
[b] T_{max}: temperature of the maximum of the endothermic effects in the DTA curve
[c] T_k: temperature of anhydrous salt formation
[d] n: amounts of crystallization water molecules

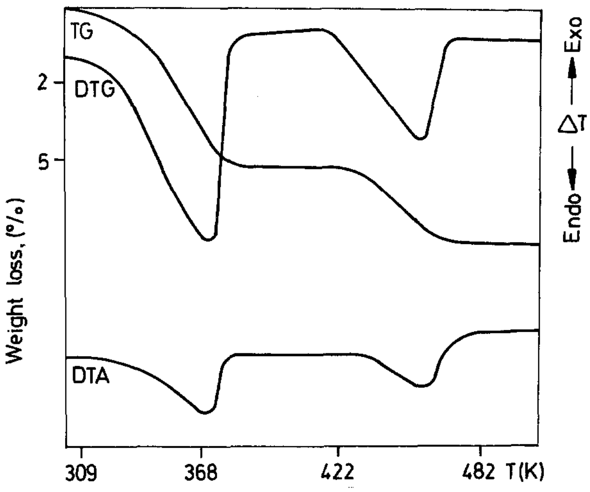

Fig. 1. TG, DTG, and DTA curves of Y $(C_7H_3O_6N_2)_3 \cdot 3H_2O$

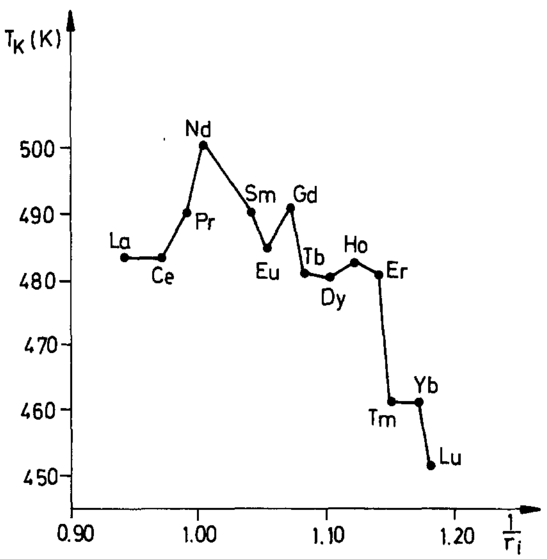

Fig. 2. Relationship between the temperature of anhydrous salt formation (T_k) and ionic potential of element ($1/r_i^a$)

the hydrated salts were observed. Accordingly, it is possible to assume that being heated in the temperature range 273–573 K all 3,5-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 the ignition of oxalates or 3,5-dinitrobenzoates of Y, La, and lanthanides).

3,5-Dinitrobenzoates of rare earth elements are stable up to 573 K after which they are explosively decomposed. Thus, their thermal stability was studied only in the temperature range 273–573 K. Some of the obtained results are presented in Table 3. Fig. 1 exhibits the derivatogram of yttrium 3,5-dinitrobenzoate. All the 3,5-dinitrobenzoates of Y, La, and lanthanides dehydrate in two steps. Connected with endothermic effects the dehydration processes proceed in the temperature ranges 303 K–431 K and 392 K–491 K. At first all trihydrates lose two water molecules, finally followed by the remaining one. In the temperature range 303 K–431 K the least thermally stable complexes are the hydrates of Pr (III), Gd, Tb,

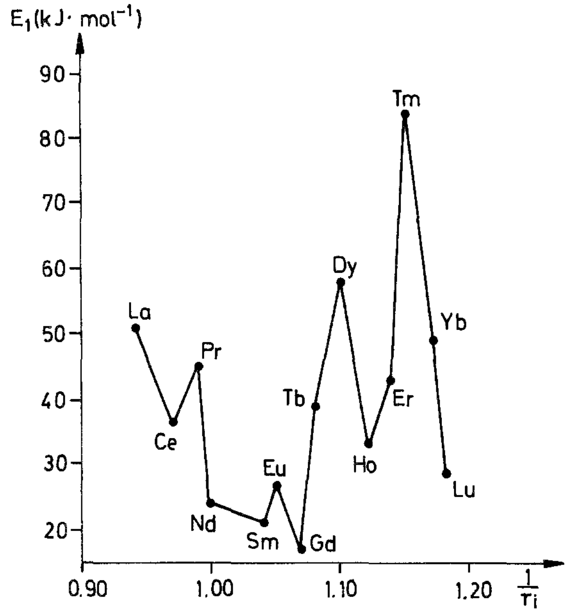

Fig. 3. Dependence between the activation energy of dehydration reaction for the loss of two water molecules of 3,5-dinitrobenzoates of rare earths (E_1) and ionic potential of element ($1/r_i^a$)

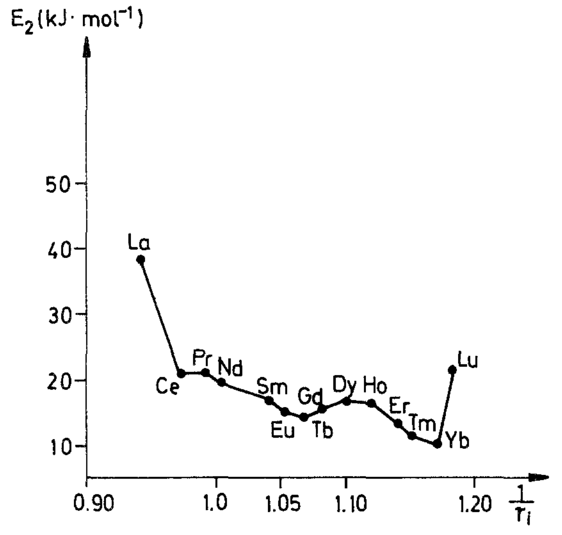

Fig. 4. Relationship between the activation energy of dehydration for the loss of one water molecule (E_2) and ionic potential of element ($1/r_i^a$)

and Lu which start to lose the crystallization water at 303 K, while the most thermally stable one is lanthanum 3,5-dinitrobenzoate which releases water molecules at 385 K. In the temperature range from 392 K to 491 K the complex of praseodymium expelling water molecules at 447 K is the most thermally stable whereas the least thermally stable is the lutetium 3,5-dinitrobenzoate starting its dehydration at 392 K. The anhydrous salts of rare 3,5-dinitrobenzoates are formed in the temperature range from 452 K (for Lu) to 501 K (for Nd).

The temperature of the anhydrous complex formation does not regularly change with the ionic potential of elements (Fig. 2, r_i-Templeton's value). Being lost at comparatively low temperatures and in two stages the water molecules seem to be outer-sphere water and probably occupy various positions in the same complex coordination sphere. From TG and DTA curves the activation energies of the

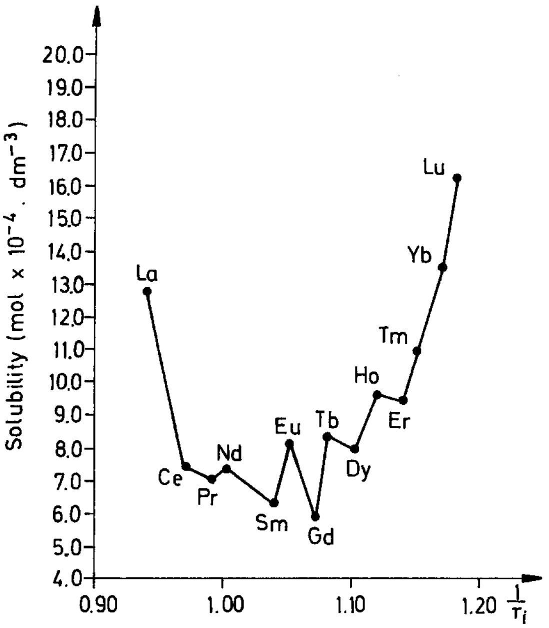

Fig. 5. Relationship between the solubilities of 3,5-dinitrobenzoates of rare earths in water and ionic potential of element ($1/r_i^a$); r_i^a – Templeton's value

dehydration reaction for 3,5-dinitrobenzoates were calculated by means of the Fateev and Pletneev method [17] (Table 3, Figs. 3, 4). The greater values of the activation energies calculated for the loss of two water molecules compared to those for the third one may suggest that water molecules (depending on their positions in the coordination sphere) are probably bound with different force. In the case of the loss of two water molecules the thulium 3,5-dinitrobenzoate shows the highest value of activation energy while gadolinum the smallest one. The activation energy connected with the loss of one water molecule is highest for the lanthanum 3,5-dinitrobenzoate and the smallest for thulium. The solubilities of 3,5-dinitrobenzoates of Y, La, and lanthanides in water at 298 K were measured and their solubility products determined (Table 3). They are in the order: 10^{-4} mol dm^{-3} and 10^{-12} mol^4 dm^{-12}, respectively. The 3,5-dinitrobenzoate of Lu is the most soluble salt while Gd is the least soluble one (Fig. 5).

The solubilities of 3,5-dinitrobenzoates of rare earth elements are smaller compared to those of 3-nitrobenzoates of the same elements [18], which is probably connected with the presence of a second nitro group in 3,5-dinitrobenzoates and its relative position in the benzene ring.

References

[1] Beilstein (1926) Handbuch der organischen Chemie, Bd. 9. Springer, Berlin, p. 167

[2] Kolthoff I. M., Chantooni M. K. (1967) J. Amer. Chem. Soc. **89**: 2521

[3] Fogel'żang A. E., Adzhemyan V. Ya., Svetlov B. S. (1980) Tr-Mosk, Khim-Tekhnol. Inst. D. J. Mendelejeva **70**: 112

[4] Madey A., Oleksyn B. J. (1986) Pol. J. Chem. **60**: 193

[5] Colter A. K., Grunwald E. (1970) J. Phys. Chem. **74**: 3637

[6] Agrawal A. P., Yoganarasimhan S. R., Agrawal I. P. (1986) Kogyo Koyaku **47**: 2

[7] Agrawal A. P., Yoganarasimhan S. R., Agrawal I. P. (1986) Def. Sci. J. **36**: 309

[8] Bikham B. I., Gurewitz M. Z., Shugal N. F., Dyatlova N. M. (1980) Zh. Neorg. Khim. **25**: 2567
[9] Shelke D. N., Jahagirdar D. V. (1976) Indian J. Chem. **14A**: 353
[10] Butin K. P., Beletskaya I. P., Belik P. N., Reutov O. A. (1969) J. Organometal. Chem. **20**: 11
[11] Grigoriev A. I., Maksimov W. N. (1964) Zh. Neorg. Khim. **9**: 1060
[12] Manhas B. S., Trikha A. K. (1982) J. Indian Chem. Soc. **2**: 315
[13] Fee W. W., Gamer C. S., Harrowfield I. N. (1967) Inorg. Chem. **6**: 1389
[14] Kukuszkin I. N. (1972) Koord. Khim. **4**: 1170
[15] Goodgame D. M. L., Hitchman H. A. (1967) Inorg. Chem. **6**: 813
[16] Nakamoto K. (1986) Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley, New York
[17] Cherchas Ch. A., Jezierskaya T. P. (1977) Izv. Akad. Nauk SSSR **1**: 45
[18] Ferenc W. (1988) Monatsh. Chem. **119**: 1345

Received May 17, 1989. Accepted June 16, 1989