Isolation and characterization of four intermediate hydrates by isothermal dehydration of $Y(OH)_x(NO_3)_{3-x} \cdot yH_2O$ ($x=1.67$; $y=2.5$)

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Abstract

Thermal dehydration of $[Y_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6](NO_3)_2 \cdot 4H_2O$ (1), simplified as $Y_6(OH)_8(NO_3)_8 \cdot 15H_2O$ (1a) or $Y(OH)_{1.67}(NO_3)_{1.33} \cdot 2.5H_2O$ (1b) occurs in five separate steps. The difference of the dehydration process in moist and dry air in the 25–220°C range was investigated by simultaneous TG–DTA. Four hydrates with an approximate composition $Y_6(OH)_8(NO_3)_8 \cdot yH_2O$ ($y=12.5$ (2), 10 (3), 8.5 (4), 6 (5)) were isolated by isothermal TG in moist atmosphere at specified temperatures and characterised by FT–IR and XRD. The reversibility of dehydration of the compounds against moist air during storage at room temperature is described. The fully dehydrated product with a good stability in the 140–380°C range was found to be $Y(OH)_x(NO_3)_{3-x}$ ($x=1.67$) (6), instead of a compound with $x=1.5$ (6a), as had been supposed and described in a previous paper [1]. An alternative way of evaluating the TG-curves, which overcame discrepancies between observed and calculated mass losses, is described. © 1997 Published by Elsevier Science B.V.

Keywords: Hydroxy-nitrate; Isothermal TG; TG-curve calculation; Thermal decomposition; Yttrium

1. Introduction

The title compound was discovered as an intermediate precipitate of the step-wise hydrolysis of thermal or chemical decomposed rare-earth nitrates – a method to enrich Y-free heavy rare-earth elements using rare-earth mixtures of natural composition as starting material [2–4]. That compound was produced in kg-quantities when using this procedure and has been established as being responsible for the efficiency of this method. The structure of $[Y_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6](NO_3)_2 \cdot 4H_2O$ (1) for several lanthanides (Ln) as the cationic part has been found to be monoclinic in case Ln=Gd and triclinic when Ln=Y, Yb with M_6X_6-clusters and an interstitial O-atom [5]. Compounds with Ln=Sm–Yb and Y, having chemical and physicochemical properties analogous to (1), have been prepared by the author. Comparable investigations for the whole row – as they are described for Ln=Y in the present paper – are in progress.

First of all, it was difficult to prepare fractions of (1) with defined water content and molecular weight, which proved to be a major problem in handling this product in kg-quantities when using this kind of separation method. The molecular weight of product (1) depended on the method of washing and drying that was used in each case, and differed by up to 6–7% in a non-reproducible way, even if samples of pure

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rare-earth elements had been prepared under well-defined conditions. At room temperature the water content changed, depending on the humidity of the atmosphere during storage. For that reason some investigations for characterising this compound as an important intermediate part of the separation method could not be done in a reliable way.

A further problem was the uncertainty of calculating the molar mass of the products by TG-analysis of (1) on the basis of the stable end product of the thermal decomposition, Y_2O_3.

2. Experimental

2.1. Preparation of the starting material (1)

The preparation was carried out with the help of a method similar to the one already described in detail by the author [1]. An amount of 50 g Y_2O_3 was dissolved in hot concentrated nitric acid and boiled gently until the solution became clear. Following that, the clear solution was heated very carefully until NO_x started to be generated ($\approx 260°C$). On becoming turbid ($\approx 300°C$), the yellow-brown melt was poured slowly into 70 ml of water and kept boiling for a further 3–4 h. The reaction is completed when a small sample of the milky suspension becomes totally soluble in water, otherwise further boiling of the solution is necessary. While boiling the suspension, the volume should not be <100 ml; the boiling temperature was $\approx 120°C$. After the reaction was completed, 20 ml of water was added to the suspension and boiled for a further 20 min; the precipitate was isolated by a scavenge pump, washed with some small portions of ice cold alcohol, and dried in an air stream. The resulting white crystalline powder was easily soluble in water, resulting in the well-known hydrolysis reaction leading to a gelatinous mass [1,2].

The Y_2O_3 used, which had a purity higher than 99.9%, was purified by liquid–liquid distribution (Craig distribution) in the tributylphosphate–HNO_3 system and analysed by emission-spectroscopy [7].

2.2. FT–IR analysis

The characterization of the solid products by IR was done with a FT–IR 6005 (Perkin–Elmer) apparatus, using the Nujol/KBr-disc technique. The KBr-pill method was not a reliable alternative because of the possible influence of high pressure on the water content of the samples.

2.3. TG–DTA experiments

Investigations with TG–DTA as well as the preparation of the defined hydrates by isothermal decomposition were carried out with a TGA850 (Mettler–Toledo) apparatus. The protective gas for the weighing unit was dry nitrogen (rate: ≈ 5 ml min^{-1}), and the purge gas for the heating unit was dry or moist air (rate: 50 ml min^{-1}); the crucibles were made of Al_2O_3 ('Alox', 70 μl). The moist atmosphere was normal air as it existed in the laboratory with a relative humidity of 50–70%. Dry air was obtained by treating it first with $CaCl_2$ (siccative) and afterwards with dry silica gel, both filled in 1 m tubes. The sample size was usually 10–20 mg for analytical, and 50–60 mg for preparative experiments. The calculations were done by the TSW870 V3.0 SCSI-DAT (Mettler–Toledo) software, the computer used was a DELL Optipex XM590M. The DTA curves were obtained indirectly by simultaneous calculation. In order to attain the calculated height of decomposition steps in a TG-curve, the on-set and off-set temperatures were automatically set by the computer programme which uses the turning points between the steps as reference (Figs. 1–3).

Especially adapted temperature runs with alternating steps of dynamic and isothermal heating rates were created for isothermal TG experiments. The selected temperatures for preparing the intermediates were low enough to avoid decomposition of the product wanted and high enough to obtain it in reasonable time at a constant weight (Fig. 3). All TG–DTA curves were calculated by subtraction of the corresponding blank curves.

2.4. X-ray powder diffraction (Guinier)

Diffraction patterns were obtained with a Huber camera (r=114.59 mm; Siemens), using monochromatic Cu $K_{\alpha 1}$ radiation (λ=0.154056 nm) with an exposure time of 5–7 h and germanium (6N) as internal standard (lattice parameter a=0.5657906 nm).
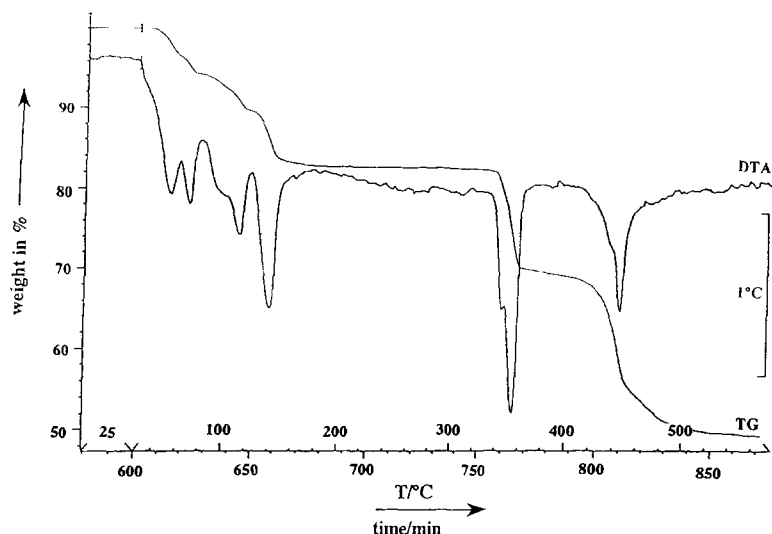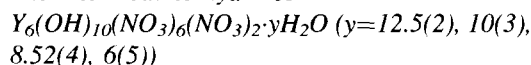
Fig. 1. TG–DTA curves for the thermal decomposition of $Y_6(OH)_{10}(NO_3)_8 \cdot 15H_2O$ (1) in humid atmosphere (purge gas rate: 50 ml min^{-1}; heating rate: 3 K min^{-1}).

3. Results and discussion

3.1. The intermediate hydrates
$Y_6(OH)_{10}(NO_3)_6(NO_3)_2 \cdot yH_2O$ (y=12.5(2), 10(3), 8.52(4), 6(5))

As already described, there is a problem that samples of compound (1) can contain a certain amount of water even at room temperature, depending on the humidity of the atmosphere. If the TG-experiments are carried out under humid conditions, the thermal dehydration of (1) occurs in five steps with a large overlapping of steps 3 and 4 and is completed at

$\sim 160°C$ (Fig. 1). Comparing DTA curves of experiments, carried out in dry and humid atmosphere, it can be seen that 'dry' dehydration occurs at temperatures $\approx 7°C$ lower than those at which 'humid' dehydration occurs. The five steps of dehydration can be better separated using humid air as purge gas (Fig. 2(b)), whereas steps 1 and 2 are overlapping in the dry atmosphere, and dehydration during steps 3 and 4 seems to be the same process (Fig. 2(a)). Therefore, the intermediate hydrates were prepared at 35, 67, 85 and 100°C using humid air as purge gas (flow rate: 50 ml min^{-1}) (Fig. 3; Table 1). Each temperature remained constant for ≈ 10 h, until no further weight loss was detectable.

Table 1
Step-wise isothermal dehydration of (1) with humid air as purge gas. In order to facilitate a comparison with (1), the formulae of the resulting intermediates are simplified as Y_6-units

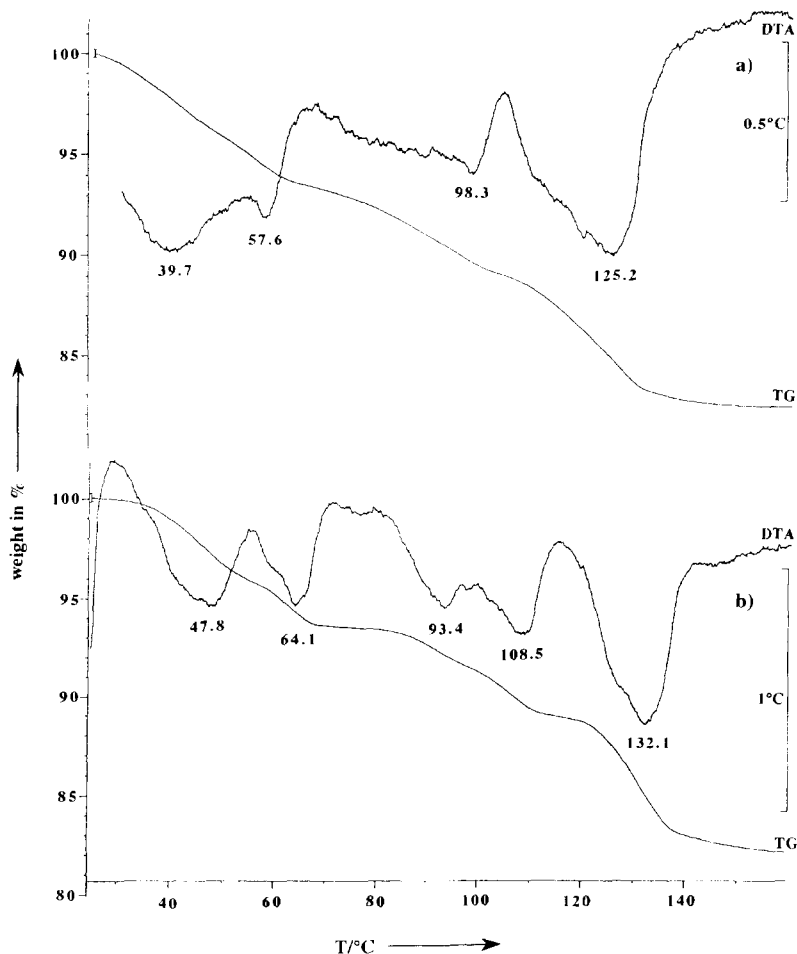| Temperature (°C)	Relative weight loss (%)		$-xH_2O$	Intermediate
	Calculated	Observed		
25	—	—		$Y_6(OH)_{10}(NO_3)_8(H_2O)_{15}$ (1)
35	−3.06	−2.78	−2.5	$Y_6(OH)_{10}(NO_3)_8(H_2O)_{12.5}$ (2)
67	−3.06	−3.43	−2.5	$Y_6(OH)_{10}(NO_3)_8(H_2O)_{10}$ (3)
85	−1.84	−1.82	−1.5	$Y_6(OH)_{10}(NO_3)_8(H_2O)_{8.5}$ (4)
100	−2.45	−2.36	−2.0	$Y_6(OH)_{10}(NO_3)_8(H_2O)_6$ (5)
180	−7.35	−7.41	−6.0	$6 \cdot [Y(OH)_{1.67}(NO_3)_{1.33}]$ (6)

Fig. 2. TG–DTA curves of thermal dehydration of $Y_6(OH)_{10}(NO_3)_8 \cdot 15H_2O$ (1) in (a) dry and (b) humid air.

An alternative method of obtaining compound (3) is to treat a small sample of (1) with dried air at room temperature for several hours. Dehydration to (3) occurs in one step, the detected weight loss corresponding exactly to the result as it was obtained by isothermal TG under humid conditions at 67°C (Table 1). As estimated from Fig. 2(a), the intermediates (2) and (4) could not be obtained by isothermal decomposition in dry atmosphere.

The comparison of the IR-spectra of (2–5) showed no significant difference from that of (1) (Fig. 4(a, b)). In relation to the original compound (1), the broad bands in the region of 770 cm^{-1} become a little more overlapped. Therefore, a dramatic change of the structure during the dehydration process is not possible

before (6) is formed. The IR-spectrum belonging to (6) shows a number of bands in the finger-print region, more than the hydrates do, e.g. one double peak at 1056.9 and 1048.4 cm^{-1}, one broad band at 875.5 cm^{-1}, two sharp peaks at 829.2 and 802.0 cm^{-1}, and a cascade of overlapping peaks with maxima at 770.5, 739.9, 705.1 and 690.9 cm^{-1} (Fig. 4). The absence of water absorption bands (at >3000 and 1634 cm^{-1}) and the sharpness of the pairs of OH-bands at 3568.0 and 3336.3 cm^{-1} confirm the analytical result obtained by calculation from the TG data as described earlier. Evidently, the cluster-like structure of (1) is independent of the water content, and is destroyed when it comes to decomposition from (5) to (6) at temperatures higher than 100°C.
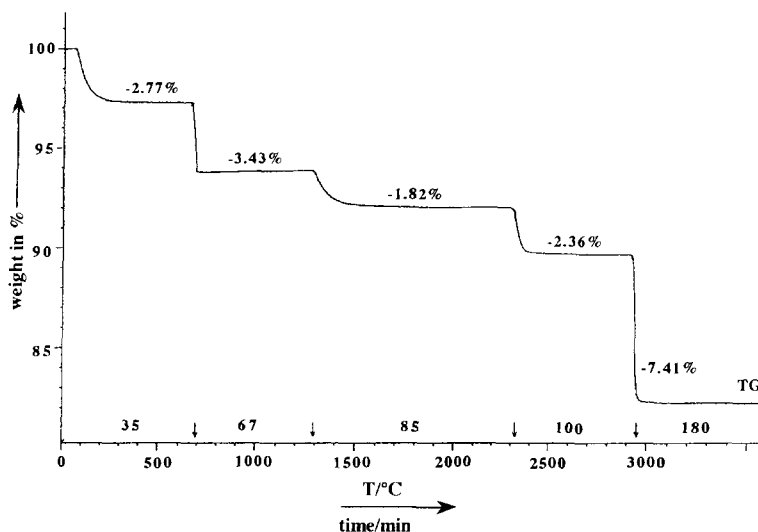
Fig. 3. TG-curves for the step-wise isothermal dehydration of $Y_6(OH)_{10}(NO_3)_8 \cdot 15H_2O$ (1) (isotherm: 35°C (10 h), 67°C (10 h), 85°C (17 h), 100°C (10 h), and 180°C (>10 h); dynamic heating rate between the isotherm steps: 5 K min^{-1}; sample mass: 17 mg; purge gas: humid air; flow rate: 50 ml min^{-1}.

The foregoing conclusion seems to be confirmed, furthermore, by XRD-examinations. The Guinier spectra of (2–5) were very similar to that of (1). The $d_{(observed)}$-characterization of the strongest signals is listed in Table 2, where (3) was taken as a representative for the other hydrates.
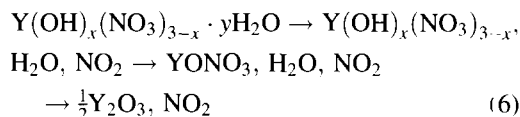
In order to obtain better knowledge of the nature of the hydrates, Rietveld- and neutron-scattering investigations are in progress.

The chemical behaviour of the compounds during hydrolysis was a further detail of interest for their characterization. In contrast to the anhydrous intermediate (6), the hydrates (2–5) are very highly soluble in water, showing exactly the same hydrolysis reaction by forming the insoluble compound $Y(OH)_2NO_3$ (7) as it is known to be very typical of (1) [1,2]. Therefore, it can be stated that dehydration of (1) does not have any significant effect on the chemical behaviour of the product.
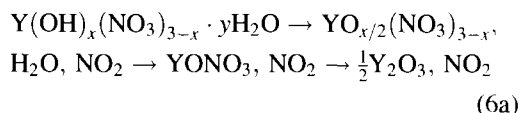
3.2. $Y(OH)_{1.67}(NO_3)_{1.33}$ (6) instead of $YO_{0.75}(NO_3)_{1.5}$ (6a)

An anhydrous intermediate with a good stability in the 180–320°C range (Fig. 1) was prepared by thermal dehydration of (1). The calculation of the formula for this compound, derived from mass losses in the

TG-curves, leads to a composition which is an oxide-nitrate rather than an hydroxy-nitrate (Table 3).

$$Y(OH)_x(NO_3)_{3-x} \cdot yH_2O \rightarrow Y(OH)_x(NO_3)_{3-x},$$
$$H_2O, NO_2 \rightarrow YONO_3, H_2O, NO_2$$
$$\rightarrow \tfrac{1}{2}Y_2O_3, NO_2 \qquad (6)$$

respectively

$$Y(OH)_x(NO_3)_{3-x} \cdot yH_2O \rightarrow YO_{x/2}(NO_3)_{3-x},$$
$$H_2O, NO_2 \rightarrow YONO_3, NO_2 \rightarrow \tfrac{1}{2}Y_2O_3, NO_2$$
$$\qquad (6a)$$

In view of the conformity between calculated and experimentally observed data for the oxide-nitrate (calculated: 71.74; observed: 70.77) by use of the oxide-evaluation method (Table 3), and the corresponding FT–IR-spectra (absence of water bands in Fig. 4(c)), (6a) became the most probable formula for this compound [1]. In that report the OH-bands were ascribed to the presence of some impurities, produced during the preparation of the IR-samples. After the preparation of single crystals of (1) had been successfully carried out, and the structure as well as the composition of Ln=Gd, Y, and Yb investigated by a four-circle diffractometer [5], it was necessary to again study the real nature of the intermediate because
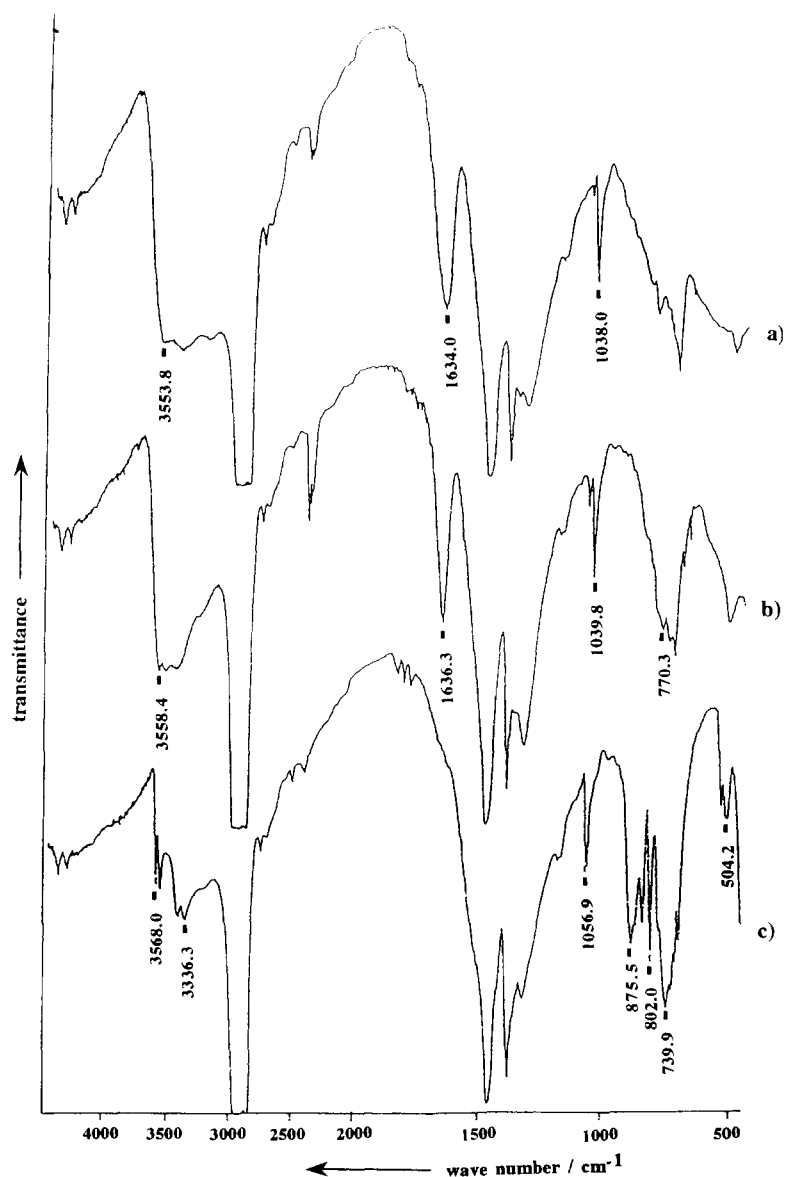
Fig. 4. FT–IR spectra (KBr/Nujol) of $Y_6(OH)_{10}(NO_3)_8 \cdot yH_2O$: (a) $y=15$ (1), (b) $y=10$ (3), and (c) $y=0$ (6).

of the existing discrepancy of the results achieved up to now.

One of the main problems in evaluating the TG curves for obtaining the molar masses of the intermediates, was the good stability of the oxide-nitrate/oxide phases, which are formed at $\approx 450°C$ (Fig. 1) [6]. It is maintained even up to 750–800°C and no constancy of weight could be noticed even after

isothermal heating at this temperature for many hours. Furthermore, the molar mass of the oxide, in relation to the estimated weight loss caused by thermal decomposition of (1), was not suitable for reliable calculations.

A more effective and reliable way to acquire better knowledge of x is the use of the ratio of the two weight-loss steps of decomposition, beginning at

Table 2

$d_{(observed)}$ for (3) as representative for the other hydrates (2, 4, 5) is listed in comparison with (1) and the dehydrated compound (6). Only the strongest signals with their estimated intensities are shown

$Y_6(OH)_{10}(NO_3)_8 \cdot 15H_2O$ (1)		$Y_6(OH)_{10}(NO_3)_8 \cdot 10H_2O$ (3)		$Y(OH)_{1.67}(NO_3)_{1.33}$ (6)	
$d_{(observed)}$ [a]	Intensity [b]	$d_{(observed)}$ [a]	Intensity [b]	$d_{(observed)}$ [a]	Intensity [b]
9.3907	sst	9.3560	sst	—	—
9.2149	sst	9.1815	sst	—	—
8.8601	st	8.7898	st	—	—
8.1102	st	8.0806	st	8.1559	st
7.9824	st	7.9147	st	—	—
—	—	—	—	7.7319	st
—	—	—	—	7.5842	st
—	—	—	—	7.3774	st
7.2105	m	7.1959	st	—	—
6.6716	m	6.6466	m	—	—
6.4256	m	6.4177	m	6.4370	m
5.3827	m	5.3762	m	—	—
—	—	—	—	4.7126	s
4.6476	m	4.6440	st	—	—
—	—	—	—	4.4872	st
—	—	—	—	4.1642	s
4.0171	m	4.0046	st	4.0805	st
3.7155	st	3.7071	st	—	—
3.6194	m	3.6108	m	—	—
3.5857	m	3.5814	m	—	—
3.4655	st	3.4595	sst	—	—
—	—	—	—	3.1623	s
—	—	—	—	3.1123	s
3.0620	st	3.0584	m	—	—
3.0189	st	3.0129	sst	—	—
—	—	—	—	2.8357	sst
2.6414	st	2.6391	sst	—	—
2.4900	st	2.4947	st	—	—
2.3076	st	2.3061	st	—	—
—	—	—	—	2.2868	m
2.1179	sst	2.1090	st	—	—

[a] Observed distances of the reflecting planes in Å.
[b] Estimated Intensities: m=medium; s=strong; sst=very strong.

Table 3

Weight difference of thermal decomposition of (1) (in %) according to Fig. 1. The comparison of the two calculation methods for x from experimental data is shown

Intermediate	$\Delta w_{calculated}$ (%)		$\Delta w_{observed}/(\%)$	x_{oxide}	x_{Δ_1/Δ_2}
	$x=1.67$	$x=1.50$			
$Y(OH)_x(NO_3)_{3-x} \cdot 2.5H_2O$	+168.22	+196.08	207.73	—	—
$Y(OH)_x(NO_3)_{3-x} \cdot H_2O$	+92.89	+95.68	+91.95	—	—
$Y(OH)_x(NO_3)_{3-x}$	+76.94	+79.72	—	1.82	1.67
$YO_{x/2}(NO_3)_{3-x}$	+63.61	+71.74	+70.77	1.52	1.39
$\frac{1}{2}Y_2O_3$	0.00	0.00	0.00	—	—

$\approx 320°$ and 400°C (Fig. 1). The little shoulder in the endothermic peak of step 1, as it can be seen in the DTA curve, indicates an overlapping of two reactions: the loss of hydroxyl water and the decomposition of nitrate. Nevertheless, the preliminary efforts of estimating the basic part x for the oxide-nitrate $YO_{x/2}(NO_3)_{3-x}$ by using the ratio of decomposition steps corresponding to the equation $x = 2 - \Delta_1/\Delta_2$, led to the result $x = 1.49$ [1].

Assuming the fully dehydrated intermediate in question is a hydroxy-nitrate and simplifying the mechanism of its thermal decomposition

$$Y(OH)_x(NO_3)_{3-x} \rightarrow YONO_3 \rightarrow \tfrac{1}{2}Y_2O_3$$
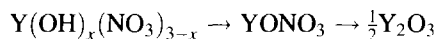
leads to the following equation for x: $x = 2.4 - 1.2(\Delta_1/\Delta_2)$ where, Δ_1 is the percentage weight loss of step 1, and Δ_2 the analogous weight loss of step 2.

Thus, the evaluation of the experimental TG-curves by use of this formula leads to $x = 1.67$ and the conclusion that the compound must be an anhydrous hydroxy-nitrate (Table 3). Moreover, this result corresponds better with the IR-spectra obtained as compared to the one discussed before, because of the definite assignment of the OH-bands (3568, 3513 cm^{-1}) to (1).

For TG-investigations of mixtures of (1) with $Y(NO_3)_3$ and/or $Y(OH)_2NO_3$ (7), when the formation of (1) was not complete after treating a melt of partially decomposed rare-earth nitrates with water [2–4], it seems important to be able to readily calculate the purity of (1) by using the ratio $\Delta_1 : \Delta_2$ (Table 4). Therefore, the degree of thermal decomposition can be estimated easily by this method as well.

Therefore, the number for the ratio $\Delta_1 : \Delta_2$ can lie between 2 and 0.334, when (7) is the precipitated product after total hydrolysis of an aqueous solution of (1). The composition of (7) was investigated by

Rietveld refinement for the analogous compound Ln=Sm as described previously [8].

It is the independence of the calculation from any starting material or an intermediate, probably with an indefinite composition, as well as the easy way of calculating its purity that makes this a preferred method. The nature of the cation of (1) need not be accounted for, and thus it can be used for all other hitherto known analogous compounds, e.g. for the lanthanides (Ln=Sm–Lu) [1,4] or for their mixtures. The decomposition/hydrolysis mechanism is always the same. Analogous investigations are in progress for the other cations.

3.3. The behaviour during storage in humid atmosphere

Storage of (1) as well as of (2–5) and (6) during several months in a humid atmosphere, as it normally exists in a laboratory (50–70% relative humidity), had no significant effect on the compositions and properties except for small variations in the water content of (1) as described earlier. In an atmosphere saturated with water at room temperature (e.g. in a closed vessel, containing a small amount of water; 100% relative humidity), the compounds hydrolysed and became a viscous solution after some days, and a mass of gelatinous consistency after some weeks. It is surprising that (6), being an anhydrous compound with characteristics different from FT–IR, XRD and solubility in water, showed the same behaviour of hydrolysis as the hydrates.

On treating a small sample of (6) at room temperature with wet air as described for ≈ 12 h and with dry air for 12 h afterwards, a product similar to (3) could be obtained. Unfortunately, the XRD-spectrum of that product was very diffuse, probably because the quality of the crystals was poor, but its characterization by TG and IR led to the same results as those of (3). Therefore, a total reversibility of dehydration over the whole range of water content (1–6) can be proposed.

Acknowledgements

Table 4
The calculated limits of x for mixtures as they will be obtained during the preparation of (1), using the ratio $\Delta_1 : \Delta_2$ for the calculations

Compound	x	$\Delta_1 : \Delta_2$
$Y(NO_3)_3$	0	2 : 1
$Y(OH)_{1.67}(NO_3)_{1.33}$ (6)	1.67	0.608 : 1
$Y(OH)_2(NO_3)$ (7)	2	0.334 : 1

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