

THERMAL INVESTIGATIONS OF DEHYDRATION OF LANTHANIDE(III) 5-NITROANTHRANILATES

*M. Sikorska-Iwan**, *Renata Mrozek*, *A. Ostasz* and *Z. Rzączyńska*

Department of General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 2, 20-031 Lublin, Poland

Abstract

The 5-nitro-2-anthranilates of lanthanum(III), samarium(III), terbium(III), erbium(III) and lutetium(III) were obtained as hydrates having 2.5 mol of water molecules per 1 mol of compound. The compounds are isostructural. The processes of dehydration and rehydration were investigated. The first step of dehydration does not cause the change of crystal structure. The entire dehydration gives anhydrous compounds with different structure than the structure of hydrates. However, the dehydration of La, Sm, Tb and Er is reversible – the rehydration process gives the complexes having the same crystal structure as the initial compounds. Only the anhydrous lutetium complex under the influence of moisture does not give the starting compound.

Keywords: dehydration, lanthanide complexes, rehydration

Introduction

For many years our research has concerned the dehydration process of lanthanide carboxylates. An interdependence between the way of thermal degradation of complexes in solid-state and their crystal structure is evident. Nevertheless, it is impossible to indicate specific structural parameters deciding about the mechanism of thermal decomposition [1]. Rather it is necessary to take into consideration the global distinction between the crystal structure of reagent and product. Hence there are quite a lot of paper in journals related to investigations of dehydration/rehydration process by use of thermal analysis and X-ray diffraction techniques, e.g. [2–4].

The preparation of lanthanide carboxylates has developed rapidly in recent years, owing to their interesting properties. As known, lanthanide ions have high affinity for hard donor atoms, and ligand containing oxygen or oxygen–nitrogen atoms may be employed to preparation of lanthanide polymeric complexes [5]. It is generally admitted that lanthanide ions present only little preference in bond direction, due to the innerness of their 4f valence orbitals [6]. The 5-nitroanthranilic acid ($C_6H_3(NO_2)(NH_2)COOH$) has several potential coordination sites and it has the high ability to form hydrogen bonds. It was the reason to our interest with structure and properties of lanthanide(III) 5-nitroanthranilates.

* Author for correspondence: E-mail: mariolas@hermes.umcs.lublin.pl

The purpose of these investigations was to observe changes in the structure of complexes proceeding during dehydration and rehydration using the isostructural series of lanthanide(III) 5-nitroanthranilates.

Experimental

The complexes of selected lanthanides(III), i.e. lanthanum, samarium, terbium, erbium and lutetium with 5-nitro-2-aminobenzoic acid (5-nitroanthranilic acid) were obtained making the lanthanide(III) chloride solution (pH 4.5) react with the solution of ammonium 5-nitroanthranilate (pH 5.5). Yellow precipitates of lanthanide(III) compounds were left for 0.5 h in solution, then filtered off, washed with water and dried at 30°C.

The contents of C, H and N were obtained by means of elemental analysis using a Perkin Elmer CHN 2400 apparatus. The crystal structures of complexes were compared in support of X-ray patterns recorded on a HZG 4 diffractometer, using Ni filtered $\text{CuK}\alpha$ radiation. Measurements were taken over the range of $2\theta=5-70^\circ$.

Thermal analysis of prepared complexes was carried out by the TG-DTA method using a Setsys 16/18 analyser (Setaram). Samples (5 mg) were heated in ceramic crucibles up to 200°C at a heating rate of $2.5^\circ\text{C min}^{-1}$ in dynamic air atmosphere ($v=0.75\text{ dm}^3\text{ h}^{-1}$).

To study the rehydration process, the samples of anhydrous compounds were held at 23°C by 120 h inside of hermetic vessel where the constant relative humidity equal 96% was kept by the aqueous solution of sulfuric acid.

Results and discussion

The complexes investigated have a formula: $\text{LnL}_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln}=\text{La(III), Sm(III), Tb(III), Er(III), Lu(III)}$; $L=\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2)\text{COO}^-$; $2.5 \leq n < 3$) (Table 1).

Table 1 Elemental analysis data of lanthanide(III) 5-nitroanthranilates ($L=\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2)\text{COO}^-$)

Compound	C/%		H/%		N/%	
	found	calcd.	found	calcd.	found	calcd.
$\text{LaL}_3 \cdot 2.8\text{H}_2\text{O}$	34.40	34.41	2.80	2.81	11.45	11.47
$\text{SmL}_3 \cdot 2.8\text{H}_2\text{O}$	33.85	33.88	2.75	2.77	11.30	11.29
$\text{TbL}_3 \cdot 2.5\text{H}_2\text{O}$	33.80	33.75	2.75	2.74	11.25	11.25
$\text{ErL}_3 \cdot 2.8\text{H}_2\text{O}$	33.15	33.12	2.70	2.71	11.00	11.04
$\text{LuL}_3 \cdot 2.6\text{H}_2\text{O}$	33.00	32.95	2.66	2.64	11.00	10.98

The compounds were dried at 30°C and next the X-ray patterns and TG/DTA curves of dehydration process were recorded. All obtained compounds are isostructural (Figs 2, 4).

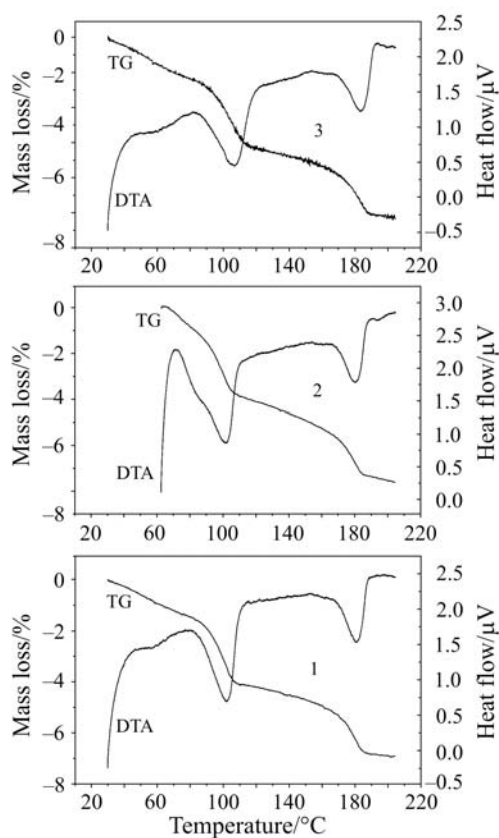


Fig. 1 TG curves of samarium(III) 5-nitroanthranilate: 1 – dried at 30°C; 2 – dried at 60°C; 3 – rehydrated

The TG curves show that dehydration proceeds in three steps (Table 2, Figs 1, 3). In the first one (30–80°C) the loosely bonded water molecules are lost. At the mentioned temperature range there are not distinct endothermic effects on the DTA curves. The X-ray diffraction patterns of initial complexes and of the partially dehydrated ones (drying at 60°C) do not show any differences. The water molecules occupy very likely the vacant lattice sites and their lost does not cause a change in crystal structure of complexes. Probably it is adsorbed water or water bonded by weak hydrogen bonds with the organic anion. The water is not bonded stoichiometrically. Its quantity amounts to about 0.5 mol per 1 mol of complex. Our previous experiments (e.g. [7, 8]) where the thermal decomposition had been compared with the crystal structure of complexes, have also shown the same results: the loss of water molecules bonded by weak hydrogen bonds has not been accompanied by sharp endothermic effect on DTA curves.

Table 2 Thermogravimetric data of the initial compounds

Stage of dehydration	I		II		III	
Temperature range/°C	30–80		80–120		140–180	
Mass loss/%	found	calcd.	found	calcd.	found	calcd.
$\text{LaL}_3 \cdot 2.8\text{H}_2\text{O}$	1.32	1.97	4.40	4.42	6.95	6.88
$\text{SmL}_3 \cdot 2.8\text{H}_2\text{O}$	1.35	1.94	4.06	4.36	6.74	6.78
$\text{TbL}_3 \cdot 2.5\text{H}_2\text{O}$	1.30	1.20	3.71	3.61	6.08	6.02
$\text{ErL}_3 \cdot 2.8\text{H}_2\text{O}$	1.50	1.89	4.10	4.26	6.67	6.62
$\text{LuL}_3 \cdot 2.6\text{H}_2\text{O}$	1.40	1.41	3.76	3.76	6.24	6.11

The following stages of dehydration take place at the ranges of 80–120 and 150–190°C. Each step is connected with the lost of 1 mol of crystallization water molecules per 1 mol of complex. In effect, the compounds undergo a complete dehydration and the anhydrous complexes are stable up to 200°C. Clear endothermic peaks on DTA curves are accompanied with each step of dehydration.

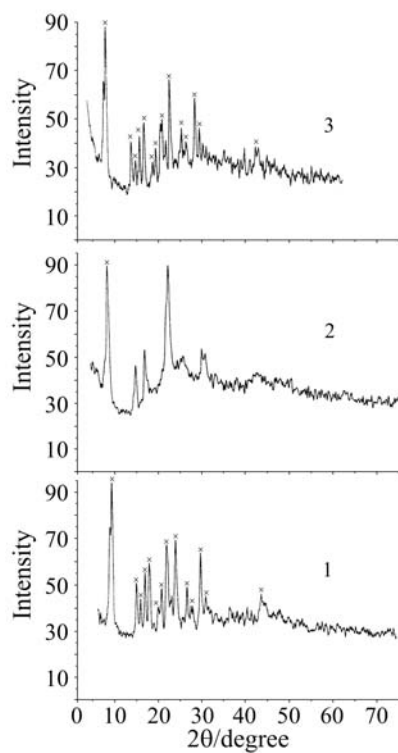


Fig. 2 X-ray patterns of samarium(III) 5-nitroanthranilate: 1 – dried at 30°C; 2 – anhydrous; 3 – rehydrated (x - reflexes appearing at the same values of 2θ)

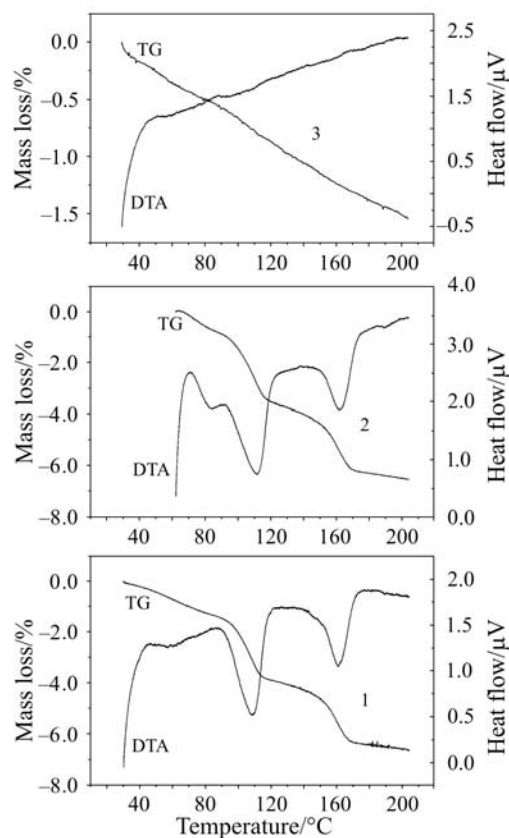


Fig. 3 TG curves of lutetium(III) 5-nitroanthranilate: 1 – dried at 30°C; 2 – dried at 60°C; 3 – rehydrated

The diffraction patterns of anhydrous complexes were recorded (Figs 2, 4). There is a distinct change of complex structure as a result of dehydration. A decrease of reflection number could testify that the structure of anhydrous compound is more arranged and the symmetry is higher compared to the initial compounds. A similar effect – lower symmetry of the hydrate in comparison with the anhydrous salt – has been observed in the case of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}/\text{CaSO}_4$ [9].

In order to check a reversibility of dehydration process the anhydrous 5-nitroanthranilates were store by 120 h at 23°C and 96% of humidity. The results of elemental analysis of rehydrates are given in Table 3. The X-ray diffraction patterns and TG-DTA curves of rehydrates were recorded. Four investigated complexes (La, Sm, Tb, Er) have rehydrated giving the initial complexes (Fig. 1). There are some little difference in the quantity of weakly bonded water molecules (Table 4). The diffraction patterns of rehydrates (Fig. 2) differ a little from the patterns of starting compounds. It is possible that time of wetting was too short and the structure has not arranged itself entirely [10, 11]. During rehydration, one has not observed the forma-

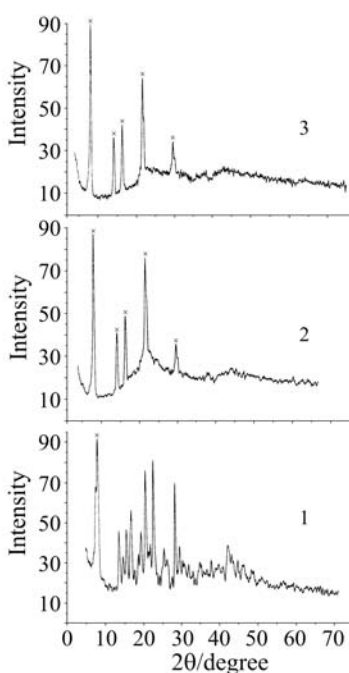


Fig. 4 X-ray patterns of lutetium(III) 5-nitroanthranilate: 1 – dried at 30°C; 2 – anhydrous; 3 – rehydrated (x - reflexes appearing at the same values of 2θ)

tion of a liquid phase – the aqueous solution of complex, as it had been observed in the case of some organic complexes of calcium [12]. The TG-DTA curves of dehydration of rehydrates were recorded. The range of temperature and the rate of dehydration do not change compared to starting complex dehydration. The same effect had been noticed by Zhu in the case of magnesium complexes [13].

Table 3 Elemental analysis data of rehydrated lanthanide(III) 5-nitroanthranilates ($L=C_6H_3(NO_2)(NH_2)COO^-$)

Compound	C/%		H/%		N/%	
	found	calcd.	found	calcd.	found	calcd.
LaL ₃ ·2.3H ₂ O	34.80	34.83	2.74	2.71	11.45	11.47
SmL ₃ ·2.2H ₂ O	34.36	34.38	2.68	2.65	11.30	11.29
TbL ₃ ·2.3H ₂ O	33.90	33.90	2.61	2.64	11.25	11.25
ErL ₃ ·2.5H ₂ O	33.36	33.36	2.61	2.65	11.00	11.04
LuL ₃ ·0.6H ₂ O	34.62	34.59	2.20	2.22	11.00	10.98

Table 4 Thermogravimetric data of the rehydrated compounds ($L=C_6H_3(NO_2)(NH_2)COO^-$)

Stage of dehydration	I		II		III	
Temperature range/°C	30–80		80–120		140–180	
Mass loss/%	found	calcd.	found	calcd.	found	calcd.
LaL ₃ ·2.3H ₂ O	0.80	0.75	3.20	3.24	5.70	5.72
SmL ₃ ·2.2H ₂ O	0.80	0.50	2.90	2.95	5.18	5.40
TbL ₃ ·2.3H ₂ O	0.60	0.73	3.00	3.15	5.50	5.57
ErL ₃ ·2.5H ₂ O	1.24	1.19	3.55	3.57	5.91	5.96
LuL ₃ ·0.6H ₂ O	30–200°C mass loss=1.5% (≈ 0.6H ₂ O)					

The lutetium 5-nitroanthranilate has not rehydrated. The TG-DTA curves recorded at the range of 30–200°C show only a strong water adsorption (Fig. 3). The X-ray diffraction pattern of rehydrate (Fig. 4) shows that the moisture has not caused changes in the structure of anhydrous compound.

Conclusions

The first step of dehydration (30–80°C) gives the hydrates with formula LnL₃·2H₂O ($Ln=La(III), Sm(III), Tb(III), Er(III), Lu(III); L=C_6H_3(NO_2)(NH_2)COO^-$). The loss of weakly bonded water molecules (lost below 80°C) does not cause change in crystal structure. Probably, there are the channels accommodating guest water molecules in the crystal structure of initial complexes.

The next steps of dehydration of lanthanide(III) 5-nitroanthranilates lead to obtain of the anhydrous compounds. Their crystal structures are different than the structures of hydrates. The increase of symmetry is observed. The rehydration gives the complexes that have the same number of coordination water molecules and the same crystal structure as the initial compounds. Only the quantity of weakly bonded water in rehydrates is less in comparison with initial hydrates.

One has failed why the lutetium(III) complex had different properties than the other investigated compounds. In this case the dehydration is irreversible. The anhydrous lutetium complex adsorbs only the moisture and it does not build the water molecules in the crystal lattice. The more stable structure of anhydrous lutetium complex compared to the other anhydrous lanthanide 5-nitroanthranilates is the reason for its different behaviour [10].

References

- 1 H. Langfelderová, J. Thermal Anal., 41 (1994) 555.
- 2 A. N. Modestov, P. V. Poplauhkin and N. Z. Lyakhov, J. Therm. Anal. Cal., 65 (2001) 121.
- 3 N. Koga, J. M. Criado and H. Tanaka, J. Therm. Anal. Cal., 67 (2002) 153.
- 4 M. Ezahri, M. El Hadek, G. Coffy and B. F. Mentzen, J. Therm. Anal. Cal., 68 (2002) 207.

- 5 R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi and Q. Shi, *Inorg. Chem.*, 41 (2002) 2087.
- 6 C. Daiguebonne, O. Guillou and K. Boubekeur, *Inorg. Chim. Acta*, 304 (2000) 161.
- 7 M. Sikorska and W. Brzyska, *J. Therm. Anal. Cal.*, 52 (1998) 505.
- 8 Z. Rzączyńska, R. Mrozek, M. Sikorska-Iwan and T. Głowiak, *J. Coord. Chem.*, 49 (2000) 189.
- 9 P. Ballirano, A. Maras, S. Meloni and R. Caminiti, *Eu. J. Miner.*, 13 (2001) 985.
- 10 R. L. Frost, J. Kristóf, E. Horváth and J. T. Kloprogge, *J. Coll. Int. Sci.*, 226 (2000) 318.
- 11 A. Alberti, G. Vezzalini, S. Quartieri, G. Cruciani and S. Bordiga, *Micropor. Mesopor. Mat.*, 42 (2001) 277.
- 12 H. J. Zhu, J. Xu, P. Varlashkin, S. Long and C. Kidd, *J. Pharm. Sci.*, 90 (2001) 845.
- 13 H. J. Zhu and D. J. W. Grant, *Int. J. Pharm.*, 215 (2001) 251.
- 14 P. Espeau, A. M. Loireau-Lozach, H. Allouchi and R. Ceolin, *J. Physique IV*, 11 (2001) 213.