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Short communication

SYNTHESIS AND THERMAL ANALYSIS OF DOUBLE OXALATES OF RARE EARTHS (III) WITH THE PYRIDINIUM CATION

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The synthesis of twelve compounds of rare earths (III) with general formula $C_5NH_6Ln(C_2O_5)_2 \times 3H_2O$ is reported. The crystals obtained were investigated by elemental and thermal analysis. At the chosen final temperature (only 400 °C), either oxide carbonate were obtained depending on the element of rare earth (III).

Key words: oxalates; rare earths (III); pyridine

INTRODUCTION

There are many data about double oxalates of rare earths (III) with a number of monovalent cations [1 – 5], but no data have been found about the double oxalates of rare earths with the pyridinium cation – $C_5NH_6^+$. Continuing our work on double oxalates of rare earths (lanthanons) with monovalent cations [6], in this paper we present the results of the preparation and characterization of double oxalates of rare earths (III) with pyridinium cation.

EXPERIMENTAL

A solution of pyridine was used for the preparation of pyridinium oxalate solution, by adding the saturated solution of oxalic acid in the molar ratio pyridine/oxalic acid = 1:1.

1.0 mol/dm^3 aqueous solution of $Ln(NO_3)_3$ were prepared, also. Double oxalates of rare earths (III) with pyridinium cation were isolated by adding 1.0 mol/dm^3 $Ln(NO_3)_3$ to a solution of pyridinium oxalate in the molar ratio 1:5, at room temperature and at pH around 6. Preliminary researches showed that a lower ratio often gives a mixture of products. The precipitate which appears immediately was filtred after 24 hours of standing, washed with water and 2% $H_2C_2O_4$ and dried in the air. The isolated double oxalates were studied by the methods of TG, DTG and DTA analysis, X-ray powder diffraction quantitative determination of C, H, N and the rare earth [7] and standard permanganometric determination of the oxalate anion.

TG, DTG and DTA curves were obtained with a Mettler's thermoanalysator with a combined TD1 measuring head, in a flow of dry air. Experimental conditions: rate of heating 4 °C/min., flow of dry air 5 l/h, mass sample about 50 mg and α-Al_2O_3 as reference material for DTA. The temperature range was from 25 to 500 °C.

RESULTS AND DISCUSSION

Analytical results, together with their calculated values, are given in Table 1. The percent of H_2O was obtained by thermogravimetrical measurements. The rasults of the quantitative chemical analysis show that these compounds have the following general empirical formula: $C_5NH_6Ln(C_2O_4)_2 \times 3H_2O$.

From the TG, DTG and DTA curves (Figs. 1 – 8), it can be seen that the thermal decomposition is similar for all compounds isolated. In the first stage of decomposition, in the temperature range from 50 °C to 130 °C, one mole of double oxalate loses three moles of water. From the second stage of thermal decomposition which begins at about 200 °C and ends at about

Table 1

Analytical data of isolated compounds

	Compound	Found (Calculated) %					
		Ln	C_2O_4	H_2O	H	C	N
1.	$(C_5NH_6)La(C_2O_4) \times 3H_2O$	29.63 (30.93)	37.68 (39.19)	11.67 (12.03)	2.79 (2.69)	24.17 (24.05)	2.79 (3.12)
2.	$(C_5NH_6)Ce(C_2O_4) \times 3H_2O$	31.02 (31.12)	40.21 (39.04)	11.71 (11.99)	2.45 (2.69)	24.58 (23.99)	2.98 (3.11)
3.	$(C_5NH_6)Pr(C_2O_4) \times 3H_2O$	31.48 (31.24)	39.79 (39.02)	11.79 (11.79)	2.88 (2.69)	24.40 (23.95)	3.33 (3.10)
4.	$(C_5NH_6)Nd(C_2O_4) \times 3H_2O$	30.91 (31.75)	38.62 (38.24)	12.89 (11.88)	2.66 (2.66)	25.01 (23.77)	3.33 (3.08)
5.	$(C_5NH_6)Sm(C_2O_4) \times 3H_2O$	31.75 (33.31)	39.33 (38.99)	12.06 (11.96)	2.31 (2.68)	25.23 (23.92)	2.75 (3.10)
6.	$(C_5NH_6)Gd(C_2O_4) \times 3H_2O$	34.27 (33.64)	38.75 (37.66)	11.06 (11.55)	2.72 (2.59)	24.32 (23.11)	3.12 (2.99)
7.	$(C_5NH_6)Tb(C_2O_4) \times 3H_2O$	34.23 (33.88)	38.34 (37.53)	12.01 (11.51)	2.31 (2.58)	23.33 (23.03)	2.87 (2.98)
8.	$(C_5NH_6)Dy(C_2O_4) \times 3H_2O$	35.51 (34.38)	38.37 (37.25)	11.00 (11.42)	2.31 (2.56)	23.33 (22.85)	2.99 (2.96)
9.	$(C_5NH_6)Ho(C_2O_4) \times 3H_2O$	33.45 (34.72)	36.96 (37.05)	10.64 (11.37)	2.93 (2.55)	23.87 (22.73)	2.87 (2.99)
10.	$(C_5NH_6)Er(C_2O_4) \times 3H_2O$	34.65 (35.04)	36.55 (36.87)	11.16 (11.31)	2.50 (2.54)	21.43 (22.62)	3.11 (2.93)
11.	$(C_5NH_6)Yb(C_2O_4) \times 3H_2O$	35.31 (35.81)	36.82 (36.43)	12.67 (11.18)	2.51 (2.51)	22.41 (22.35)	2.87 (2.84)
12.	$(C_5NH_6)Y(C_2O_4) \times 3H_2O$	20.36 (20.28)	45.07 (44.11)	13.04 (13.53)	3.19 (3.04)	27.34 (27.07)	3.69 (3.54)

300 °C, it can be conclude that one mole of pyridinium oxalate is evolved in one step, which is followed with an endothermic peak at 200 °C for La, 210 °C (Ce), 265 °C (Pr, Nd), 300 °C (Tb, Er), 295 °C (Dy) and 250 °C (Ho). Mass loss: found from TG curve 26.84 %, calculated for one mole of pyridinium oxalate, 27.66 % (La), Ce (found 28.17 %, calculated value 27.57 %), Pr (found 26.26 %, calculated 27.52 %), Nd (found 26.94 %, calculated 27.32 %), Tb (found 26.30 %, calculated 26.98 %), Dy (found 26.00 %, calculated 26.77 %), Ho (found 26.20 %, calculated 26.13 %), Er (found 25.88, calculated 26.00 %).

In the third stage, which takes place from 300 – 400 °C, the exothermic decomposition of the anhydrous oxalate of rare earth occurs. The final product of thermal decomposition at 400 °C ± 15 °C is either oxide or oxide carbonate, depending on the element of rare earth (III). This was confirmed by the theoretical values and experimental results. The experimental and calculated values for mass losses (Δm) for the final product are given in Table 2. This type of oxide carbonate ($Ln_2O \times 2CO_3$ or $Ln_2O_3 \times 2CO_2$) has also been obtained by other authors [8, 9, 10]. An exception is the decomposition of cerium pyridinium oxalate where this maximum is reached at 290 °C, probably because of the formation of CeO_2.

Table 2.

TG analysis of $(C_5NH_6)Ln(C_2O_4)_2 \cdot 3H_2O$

	Ln	t [°C]	Effect fragment	$\Delta m_{exp.}$ [%]	$\Delta m_{calc.}$ [%]
1.	La	425	La_2O_3	61.48	63.73
2.	Ce	290	CeO_2	61.37	61.37
3.	Pr	415	Pr_2O_3	58.56	58.94
4.	Nd	385	Nd_2O_3	62.78	62.97
5.	Sm	385	Sm_2O_3	61.89	61.37
6.	Gd	395	$Gd_2O \times 2CO_3$	51.98	51.62
7.	Tb	395	$Tb_2O \times 2CO_3$	49.71	51.62
8.	Dy	400	$Dy_2O \times 2CO_3$	53.01	51.23
9.	Ho	400	$Ho_2O \times 2CO_3$	51.46	50.96
10.	Er	385	$Er_2O \times 2CO_3$	50.59	50.72
11.	Yb	400	Yb_2O_3	59.01	59.01
12.	Y	395	Y_2O_3	71.70	75.00

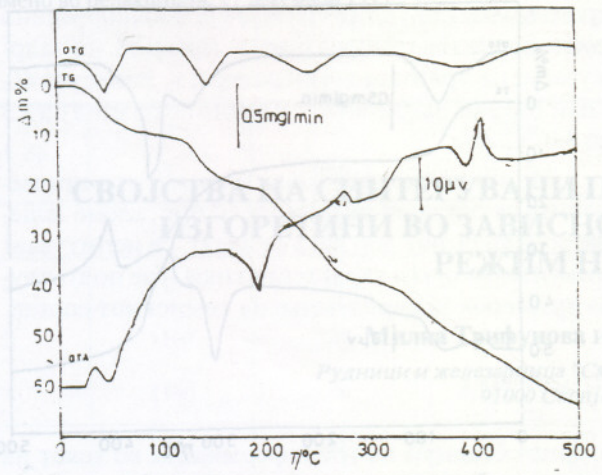

Fig. 1. TG, DTG and DTA curves of $C_5NH_6La(C_2O_4)_2 \cdot 3H_2O$

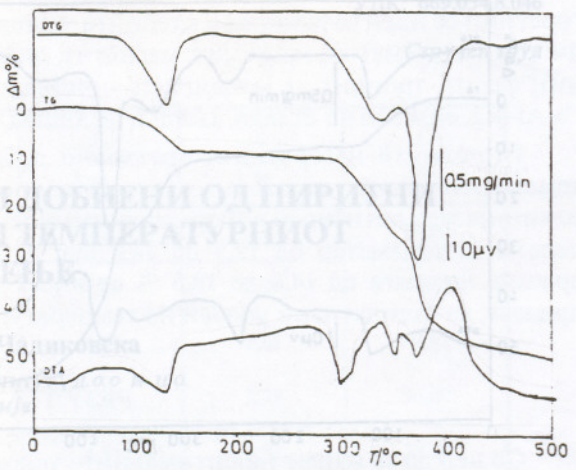

Fig. 4. TG, DTG and DTA curves of $C_5NH_6Nd(C_2O_4)_2 \cdot 3H_2O$

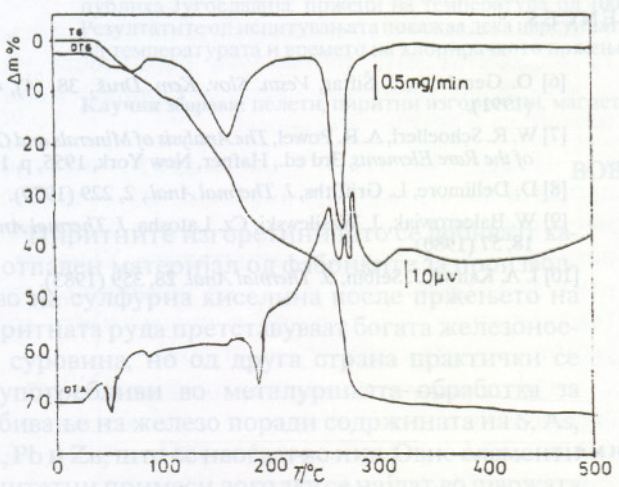

Fig. 2. TG, DTG and DTA curves of $C_5NH_6Ce(C_2O_4)_2 \cdot 3H_2O$

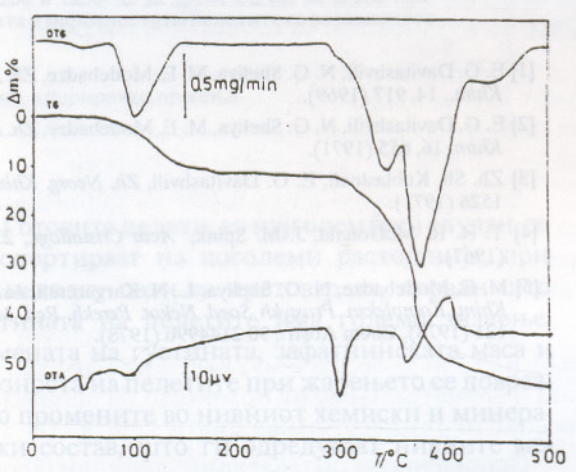

Fig. 5. TG, DTG and DTA curves of $C_5NH_6Tb(C_2O_4)_2 \cdot 3H_2O$

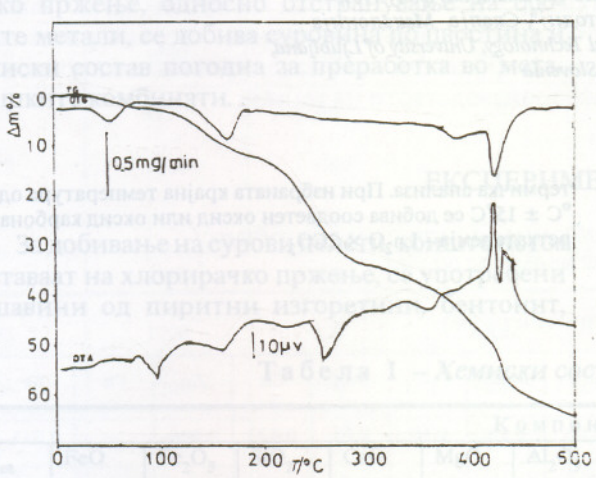

Fig. 3. TG, DTG and DTA curves of $C_5NH_6Pr(C_2O_4)_2 \cdot 3H_2O$

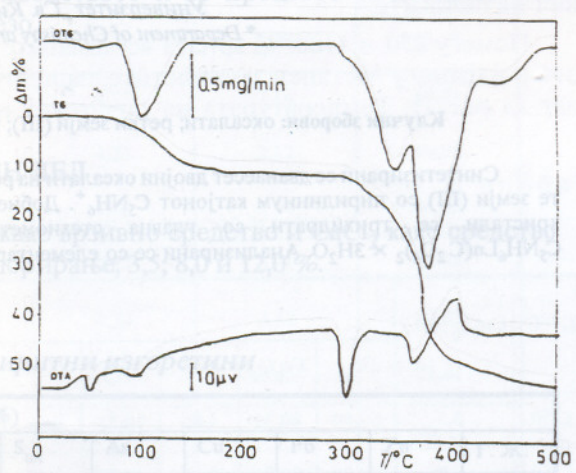

Fig. 6. TG, DTG and DTA curves of $C_5NH_6Dy(C_2O_4)_2 \cdot 3H_2O$

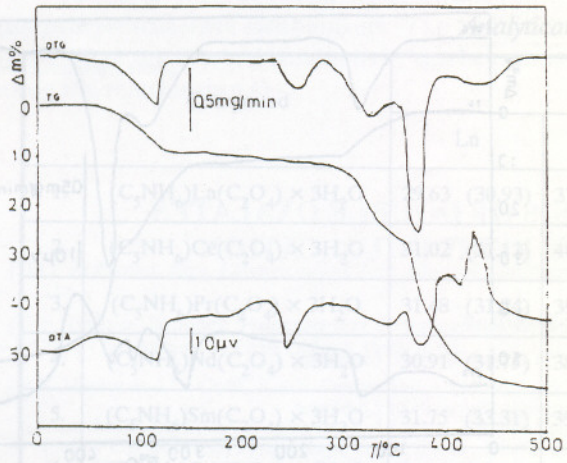

Fig. 7. TG, DTG and DTA curves of $C_5NH_6Ho(C_2O_4)_2 \cdot 3H_2O$

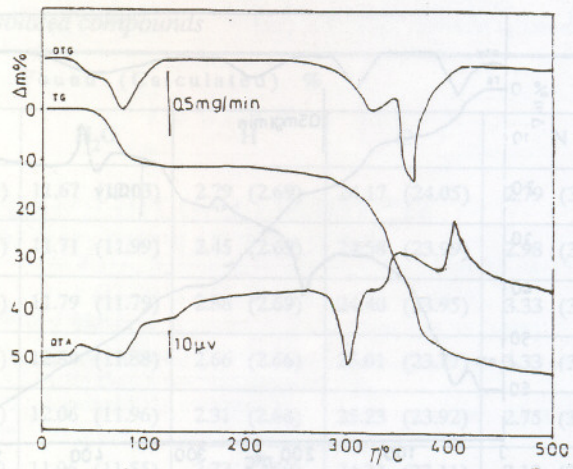

Fig. 8. TG, DTG and DTA curves of $C_5NH_6Er(C_2O_4)_2 \cdot 3H_2O$

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Резиме

СИНТЕЗА И ТЕРМИЧКО ИСПИТУВАЊЕ НА ДВОЈНИ ОКСАЛАТИ НА РЕТКИТЕ ЗЕМЈИ (III) СО ПИРИДИНИУМ КАТЈОНОТ $C_5NH_6^+$

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Клучни зборови: оксалати; ретки земји (III); пиридин

Синтетизирани се дванаесет двојни оксалати на ретките земји (III) со пиридиниум катјонот $C_5NH_6^+$. Добиените кристали се трихидрати со главна стехиометрија: $C_5NH_6Ln(C_2O_4)_2 \times 3H_2O$. Анализирани се со елементарна и термичка анализа. При избраната крајна температура од 400 °C ± 15°C се добива соодветен оксид или оксид карбонат на ретката земја – $Ln_2O \times 2CO_3$