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HYDRAZINIUM OXALATOMETALLATES OF RARE EARTHS(III)

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Abstract

Oxalates of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) with the hydrazinium cation $N_2H_5^+$ with the general formulae $(N_2H_5)_4Ln_2(C_2O_4)_5\cdot 7H_2O$ (Ln=La^{3+}, Ce^{3+}, Pr^{3+}) and $N_2H_5Ln(C_2O_4)_2\cdot 3.5H_2O$ (Ln=Nd^{3+}, Sm^{3+}) were synthesized. The thermal decompositions of these compounds take place in three stages: thermal dehydration at 65–100°C, exothermic decomposition of the N_2H_4 at 230–260°C, and oxidation of the oxalate ion.

Keywords: double oxalates, hydrazine, rare earths (lanthanons)

Introduction

The reported work is a part of continuous research in our laboratory on oxalatometallates of rare earths(III) with monovalent cations [1–4]. The present investigations relate to the double oxalates of some rare earths(III) with the monovalent hydrazinium cation $N_2H_5^+$.

Experimental

A solution of 80% N_2H_4 was used to prepare hydrazinium oxalate solution, by adding a saturated solution of oxalic acid in the molar ratio N_2H_4:$H_2C_2O_4$=1:1. 1.0 mol dm^{-3} aqueous solutions of $Ln(NO_3)_3$ were also prepared. Double oxalates of rare earths(III) with the hydrazinium cation were isolated by adding 1.0 mol dm^{-3} $Ln(NO_3)_3$ to a solution of hydrazinium oxalate in a molar ratio of 1:5 at room temperature and at pH around 6. Preliminary research showed that a lower ratio often gives mixtures of products. The precipitate which appeared immediately was filtered off after 24 h of standing, washed with ethanol and dried in the air. The isolated double oxalates were studied by the methods of TG, DTG and DTA analysis, and X-ray powder diffraction. The rare earths were determined by a standard method [5]. The sum of the oxalate anion and hydrazine was determined with the standard perman-

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Table 1 Analytical data on isolated compounds

Compound	Found (Calculated)/%					
	Ln	C_2O_4	H_2O	H	C	N
$(N_2H_5)_4La_2(C_2O_4)_5\cdot7H_2O$	28.21 (28.46)	12.62 (13.13)	12.44 (12.91)	2.69 (3.52)	11.91 (12.32)	11.39 (11.49)
$(N_2H_5)_4Ce_2(C_2O_4)_5\cdot7H_2O$	28.64 (28.39)	13.10 (12.64)	13.11 (12.88)	3.51 (3.51)	12.03 (12.26)	11.49 (11.44)
$(N_2H_5)_4Pr_2(C_2O_4)_5\cdot7H_2O$	28.71 (28.76)	12.77 (13.08)	13.19 (12.86)	3.49 (3.50)	12.34 (12.24)	11.40 (11.43)
$N_2H_5Nd(C_2O_4)_2\cdot3.5H_2O$	34.02 (34.65)	7.15 (7.94)	16.35 (15.83)	2.69 (2.91)	11.26 (11.52)	6.47 (6.72)
$N_2H_5Sm(C_2O_4)_2\cdot3.5H_2O$	35.12 (35.59)	7.72 (6.99)	15.92 (14.91)	2.75 (2.87)	11.04 (11.36)	6.83 (6.63)

ganometric method. The content of hydrazine in the double hydrazinium oxalatometallates was also determined potentiometrically with a standard solution of potassium iodate KIO_3 [6]. Elemental analyses for carbon and hydrogen were performed by Liebig's method and a carbon-hydrogen analyser (Coleman model 33), and nitrogen was analysed by the Dumas method.

TG, DTG and DTA curves were obtained with a Mettler's thermoanalyser with a combined TD1 measuring head, in a flow of dry air. Experimental conditions: rate of heating 4°C min^{-1}, flow of dry air 5 l h^{-1}, mass of 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 the calculated values, are given in Table 1. The percentages of H_2O were obtained by means of thermogravimetric measurements. The results of the quantitative chemical analysis showed that these compounds have the following general empirival formulae: $(N_2H_5)_4Ln_2(C_2O_4)_5{\cdot}7H_2O$ (*Ln*=La^{3+}, Ce^{3+}, Pr^{3+}) and $N_2H_5Ln(C_2O_4)_2{\cdot}3.5H_2O$ (*Ln*=Nd^{3+}, Sm^{3+}).

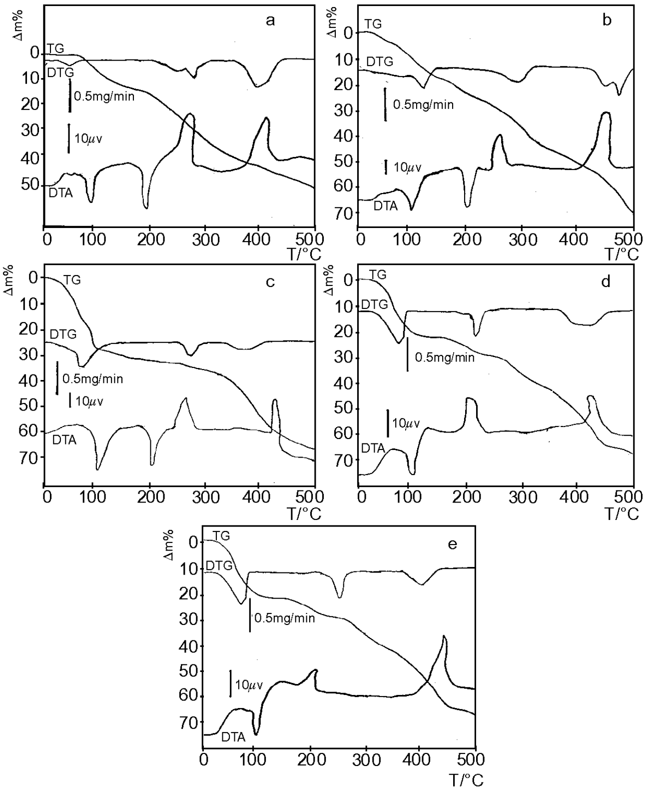

Fig. 1 TG, DTG and DTA curves $(N_2H_5)_4Ln_2(C_2O_4)_5{\cdot}7H_2O$ (La (a), Ce (b), Pr (c)), $N_2H_5Ln(C_2O_4)_2{\cdot}3.5H_2O$ (Nd (d), Sm (e))

From the TG, DTG and DTA curves (Figs 1(a)–(e)), it can be seen that the thermal decomposition is similar for all isolated compounds. In the first stage of decomposition, the complexes lose all their water in a single stage, with an endothermic peak at 95°C (La) or 100°C (Ce, Pr, Nd. Sm). From the second stage of thermal decomposition of $N_2H_5Ln(C_2O_4)_2{\cdot}3.5H_2O$ (*Ln*=Nd, Sm), it can be concluded that one mole of N_2H_4 is evolved in one step, which is accompanied by an exothermic peak at 200 (Nd) or 180°C (Sm). Mass loss: found from TG curve 7.81%, calculated 7.69% for one mole of N_2H_4 (Nd), for (Sm) found 7.66%, calculated 7.58%. In the case of $(N_2H_5)_4Ln_2(C_2O_4)_5{\cdot}7H_2O$ (*Ln*=La, Ce, Pr), it is not possible to identify intermediate compounds, so it can be concluded that four N_2H_4 moles are evolved in one step, which is accompanied by an exothermic peak at 250°C (La), 260°C (Ce) or 230°C (Pr). In the temperature range from 100 to 280°C, there is a horizontal section in the TG curve, but the DTA curve shows an endothermic peak at 200°C. This endothermic peak probably reflects the transition of $(N_2H_5)_2C_2O_4$ to $N_2H_5HC_2O_4$ [7]. The thermal properties of $(N_2H_5)_2C_2O_4$ were studied by Gajapati *et al.* [7], who found that N_2H_4 reacted with oxalic acid to form two salts, $(N_2H_5)_2C_2O_4$ at room temperature and $N_2H_5HC_2O_4$ with hot solution, whereas double oxalates and a solution of $(N_2H_5)_2C_2O_4$ were obtained at room temperature.

In the third stage, which takes place from 300 to 500°C, the exothermic decomposition of the anhydrous rare earth oxalate occurs. The X-ray powder diffraction pattern of the residue confirms that at 400±15°C it is the oxide carbonate (Ln_2O_3). One exception is the compound of La, where the oxide carbonate $Ln_2O_2CO_3$ is formed (mass loss found from the TG curve 61.78%, calculated for $La_2O_2CO_3$ 62.04%). This type of oxide carbonate ($Ln_2O_2CO_3$ or $Ln_2O_3CO_2$) has also been observed by other authors [8–10].

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