

# SYNTHESIS AND THERMAL CHARACTERISTICS OF CAESIUM OXALATO-METALLATES OF SOME RARE EARTHS

O. Genčova<sup>1</sup> and J. Šiftar<sup>2</sup>

<sup>1</sup>Institute of Chemistry, Faculty of Science, 'St. Cyril and Methodius' University, 91000 Skopje, Macedonia

<sup>2</sup>Department of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

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## Abstract

The title compounds were studied by thermogravimetry and differential thermal analysis in flowing dry air, in the temperature range 25–500°C, at a heating rate of 4 deg·min<sup>-1</sup>. Thermal analysis revealed two principal effects: dehydration, with the probable formation of a monohydrate, and oxidation of the oxalate ion at around 400°C.

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

## Introduction

A survey of the literature has not produced any substantial data on oxalato-metallates of rare earths with caesium. Davitashvili *et al.* [1] reported the isolation and thermal decomposition of CsYb(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·1.5H<sub>2</sub>O, and also the synthesis of CsSm(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and CsHo(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·*n*H<sub>2</sub>O [2–4].

Similar papers deal with the compounds CsEu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·*n*H<sub>2</sub>O [5] and CsGd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·*n*H<sub>2</sub>O [6].

We recently reported a synthesis of caesium oxalato-lanthanates:

Cs<sub>4</sub>Ln<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>5</sub>·8H<sub>2</sub>O (*Ln*=La and Pr), CsLn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (*Ln*=Nd and Sm) and CsLn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·1.5H<sub>2</sub>O (*Ln*=Gd, Tb and Dy). In a further investigation of these complexes, we have now established the conditions of the synthesis, determined the isostructural groups and investigated the thermal behaviour of all isolated compounds.

## Experimental

### Procedure

Compounds were isolated by adding saturated solutions of caesium oxalate to 1 M solutions of Ln(NO<sub>3</sub>)<sub>3</sub> at room temperature. The precipitate, which ap-

Table 1 Analytical data on the compounds and calculated values

| Compound  | Found / % |                               |                  | Calculated / % |                               |                  |       |
|---|-----------|-------------------------------|------------------|----------------|-------------------------------|------------------|-------|
|   | Ln        | C <sub>2</sub> O <sub>4</sub> | H <sub>2</sub> O | Ln             | C <sub>2</sub> O <sub>4</sub> | H <sub>2</sub> O | Cs    |
| 1. Cs <sub>4</sub> La <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>5</sub> ·8H <sub>2</sub> O | 19.78     | 32.75                         | 10.89            | 19.94          | 31.58                         | 10.33            | 38.15 |
| 2. Cs <sub>4</sub> Pr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>5</sub> ·8H <sub>2</sub> O | 20.47     | 32.28                         | 10.56            | 20.17          | 31.49                         | 10.30            | 38.04 |
| 3. CsNd(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O                             | 24.54     | 31.24                         | 19.52            | 25.70          | 31.36                         | 19.25            | 23.68 |
| 4. CsSm(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O                             | 26.91     | 30.35                         | 18.73            | 26.51          | 31.02                         | 19.04            | 23.43 |
| 5. CsGd(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O                           | 32.44     | 35.34                         | 4.94             | 31.89          | 35.69                         | 5.47             | 26.95 |
| 6. CsTb(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O                           | 31.97     | 34.72                         | 5.18             | 32.12          | 35.57                         | 5.45             | 26.86 |
| 7. CsDy(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O                           | 31.74     | 34.81                         | 5.72             | 32.60          | 35.31                         | 5.42             | 26.67 |
| 8. CsLu(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·0.5H <sub>2</sub> O                           | 35.08     | 36.46                         |                  | 35.49          | 35.71                         | 1.83             | 26.96 |

pears immediately, was filtered off after standing for 24 h, washed with water and dried in air. Rare earths were determined by the standard method [7]. Oxalate ion was determined by the permanganate method.

### Methods

The thermoanalytical curves were obtained with a Mettler thermoanalyser [8] in a flow of dry air, using a Pt/Pt-Rh thermocouple and Pt crucibles (TD1). Experimental conditions: rate of heating  $4 \text{ deg}\cdot\text{min}^{-1}$ , dry air  $5 \text{ l}\cdot\text{h}^{-1}$ , mass 50 mg, and  $\alpha\text{-Al}_2\text{O}_3$  as the reference material for DTA. The temperature range was from 25 to  $500^\circ\text{C}$ . Powder photographs for all isolated compounds were obtained with a Guinier-de Wolf camera with  $\text{CuK}_\alpha$  radiation.

### Results and discussion

At higher values of  $pH$  and when the concentration of oxalate ion was too low, mixtures of normal oxalates with oxalato-metallates were detected. In accordance with the results of preliminary investigations, the following conditions were used:  $pH$  around 6, and a molar ratio  $\text{M}_2\text{C}_2\text{O}_4/\text{Ln}^{3+}$  not lower than 5. All other conditions and the procedure have been described previously [9].

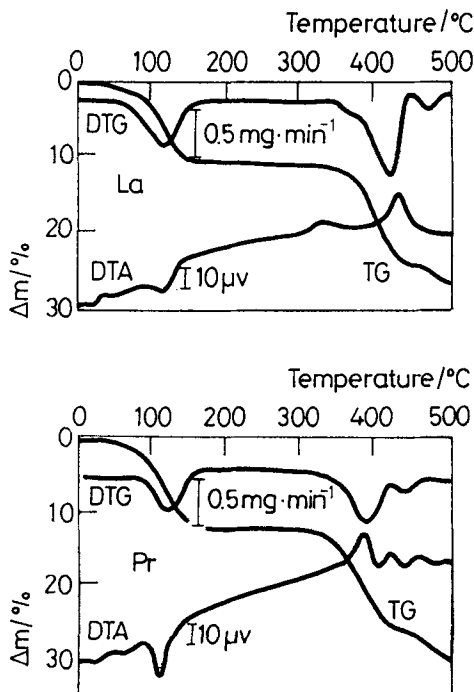


Fig. 1 TG, DTG and DTA curves of  $\text{Cs}_4\text{Ln}_2(\text{C}_2\text{O}_4)_5\cdot 8\text{H}_2\text{O}$  in air

Analytical results are given in Table 1, together with calculated values. The percentage of H<sub>2</sub>O was obtained by thermogravimetric measurements. The compounds in Table 1 were isolated at a molar ratio  $\text{Cs}_2\text{C}_2\text{O}_4/\text{Ln}^{3+} = 5:1$ . The first thing which has to be stressed as concerns the tabulated results is that another stoichiometry appears for La and Pr at a ratio  $\text{Ln}^{3+}/\text{C}_2\text{O}_4^{2-}$  of 2:5. terba-Böhn observed the same ratio only for Ce. With other rare earth elements the ratio  $\text{Ln}^{3+}/\text{C}_2\text{O}_4^{2-} = 1:2$  appears.

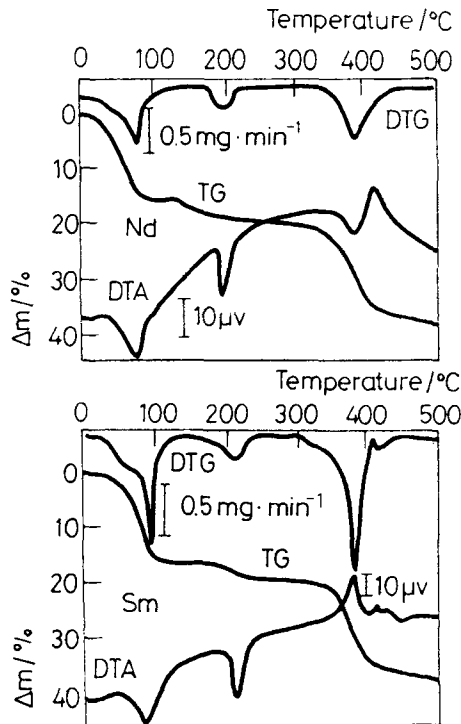


Fig. 2 TG, DTG and DTA curves of  $\text{CsLn}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  in air

All the samples were extremely dispersed and therefore the powder patterns were not very sharp. From the X-ray powder diffraction patterns, it was concluded that there are four structurally different groups: one involving La and Pr, the second Nd and Sm, the third Gd, Tb and Dy, and the fourth Lu. For more details, single-crystal structures of the representatives of all four groups will be needed.

The TG, DTG and DTA curves in Figs 1–3 show that the thermal decomposition of the double oxalates takes place in two clearly separated stages. The first corresponds to dehydration of the double oxalate. The TG, DTG and DTA curves of the double salts of La, Pr and Gd reveal that dehydration occurs in a

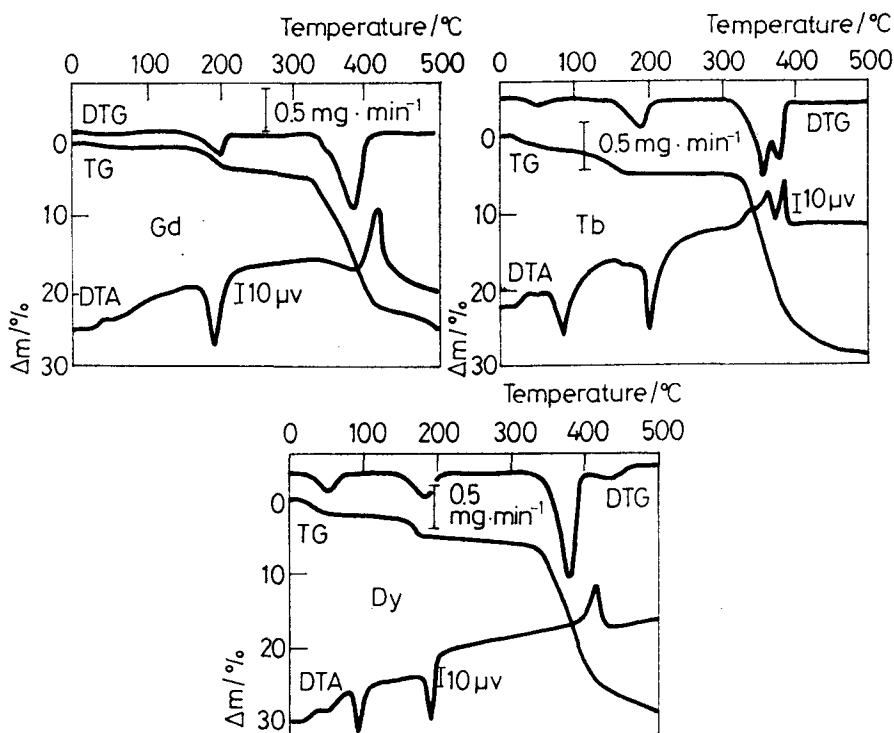


Fig. 3 TG, DTG and DTA curves of  $\text{CsLn}(\text{C}_2\text{O}_4)_2 \cdot 1.5\text{H}_2\text{O}$  in air

single endothermic process, which is followed by a single endothermic peak at 130°C for La, 115°C for Pr and 195°C for Gd. Dehydration of the Sm, Nd, Tb and Dy compounds occurs in a stepwise manner. In the first step, one mole of the double oxalates of Sm, Nd and Tb loses 5 moles of water in the temperature range 25–100°C, represented by the endothermic peak at 75°C in the DTA curves. One mole of the double oxalates of Tb and Dy loses 0.5 mole of water (endothermic peak at 95°C in the DTA curves), and the intermediate  $\text{CsLn}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  decomposes with loss of the remaining mole of water in the temperature range 100–200°C, as shown by the endothermic peak at 200°C in the DTA curves. Here, the isolation of monohydrates would probably be possible.

The second exothermic stage represents the oxidation of oxalate into a carbonate or  $\text{CO}_2$ , and also decomposition of a carbonate or basic carbonate of the rare earth into a mixture of  $\text{Ln}_2\text{O}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$ . One exception is the compound of Dy, where a mixture of  $\text{Dy}_2\text{O}_3$  and  $\text{Cs}_2\text{CO}_3$  (calculated value 29.89%, found 28.79%) is obtained.

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**Zusammenfassung** — Die Titelverbindung wurde mittels TG und DTA in strömender trockener Luft im Temperaturbereich 25–500°C und einer Aufheizgeschwindigkeit von 4 deg/min untersucht. Die Thermoanalyse ergab zwei grundlegende Effekte: die Dehydratation mit der möglichen Bildung von Monohydrat und die Oxidation des Oxalat-Ions bei etwa 400°C.