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# THERMAL ANALYSIS OF COMPLEX SALTS OF LANTHANIDE CHLORIDES WITH HEXAMETHYLENETETRAMINE

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## ABSTRACT

Thermal decomposition of lanthanide chloride complex salts with hexamethylenetetramine of the general formula $LnCl_3 \cdot 2HMTA \cdot nH_2O$ (Ln = La, Pr, Nd, Sm, Dy, Er; HMTA = hexamethylenetetramine, $N_4(CH_2)_6$; $n = 8$, 10, 12) has been examined. Mechanisms of the thermal dehydration reaction of these salts have been established and kinetic parameters of the first state of the dehydration reaction have been determined.

## INTRODUCTION

In the previous work [1] we presented the preparation of new complex salts of lanthanide chlorides with hexamethylenetetramine of the general formula $LnCl_3 \cdot 2HMTA \cdot nH_2O$ (Ln = La, Pr, Nd, Sm, Dy, Er; HMTA = hexamethylenetetramine; $n = 8$, 10, 12). The stoichiometric composition of the obtained salts with different hydration states was established and IR and Raman spectra were examined. In the present work thermal examinations have been carried out; mechanisms of the thermal dehydration reaction have been determined; the reaction order ($n$) and the activation energy of the dehydration reaction ($E_a$) have been calculated. As a result of the thermal decomposition of the salts, anhydrous salts have been obtained.

## EXPERIMENTAL

### *Thermal analysis*

A MOM derivatograph (Hungary) type OD-102 was used. Thermal curves were obtained in the temperature range 20–1000 °C in air at a heating rate of 2.5° $min^{-1}$. TG sensitivity was 100 mg, DTA and DTG sensitivity was 1/10, $\alpha$-$Al_2O_3$ was used as reference material. The analysis of 12-, 10- and 8-hydrous salts was performed by means of a derivatograph. Thermal curves

TABLE 1

Data from the thermal curves of the salts of the general formula $LnCl_3 \cdot 2HMTA \cdot 12H_2O$ (Ln = La, Pr, Nd)

| Compound | DTG peak temp. (°C) | DTA peak temp. (°C) | Peak | Mass loss on the TG curve (%) |
|---|---|---|---|---|
| $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ | 65 | 68 | Endothermic | 21.5 |
| | 130 | 125 | Endothermic | 29 |
| | | 210 | Exothermic | – |
| $PrCl_3 \cdot 2HMTA \cdot 12H_2O$ | 50 | 50 | Endothermic | 9 |
| | 85 | 80 | Endothermic | 24.5 |
| | 135 | 90 | Endothermic | 29.5 |
| | | 200 | Exothermic | – |
| $NdCl_3 \cdot 2HMTA \cdot 12H_2O$ | 50 | 50 | Endothermic | 8 |
| | 92 | 85 | Endothermic | 25 |
| | 100 | 100 | Endothermic | 29 |
| | | 210 | Exothermic | – |

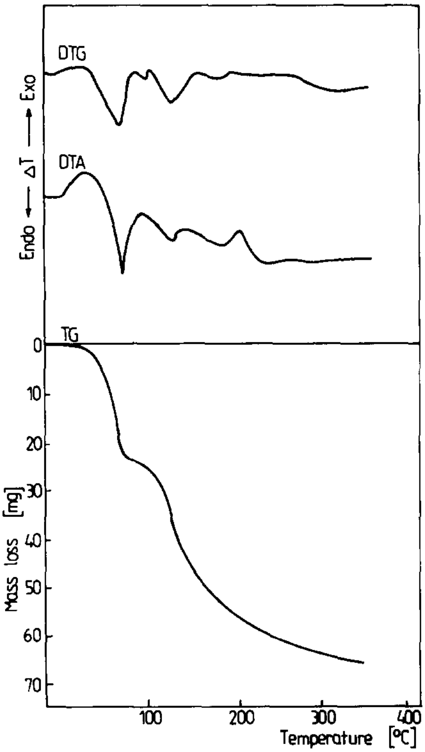

Fig. 1. Thermal analysis of $LaCl_3 \cdot 2HMTA \cdot 12H_2O$.

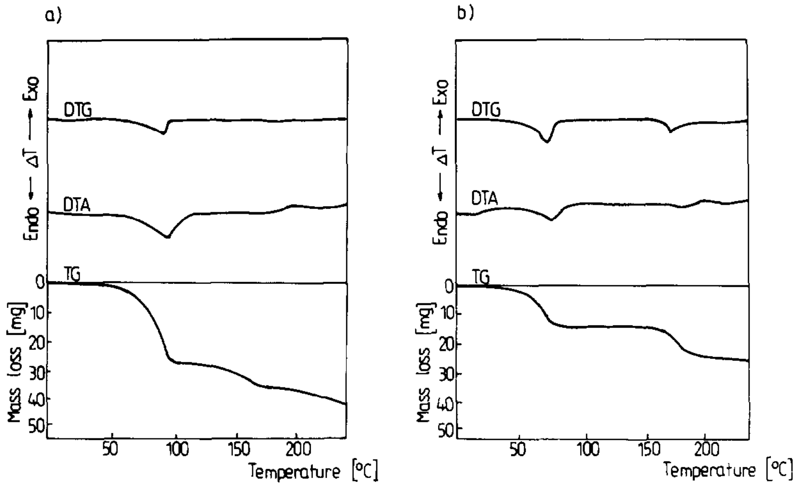

Fig. 2. (a) Thermal analysis of $LaCl_3 \cdot 2HMTA \cdot 10H_2O$. (b) Thermal analysis of $LaCl_3 \cdot 2HMTA \cdot 8H_2O$.

of the salts of the general formula $LnCl_3 \cdot 2HMTA \cdot 12H_2O$ (where Ln = La, Pr, Nd, Gd, Dy, Er) indicate that the dehydration of the lanthanum salt is a two-stage, and of the other salts a three-stage, process. The peaks on the DTG curves correspond with the mass losses observed on the TG curves, and the peaks on the DTA curves indicate that these processes are endothermic. The third dehydration stage of praseodymium, neodymium, gadolinium, dysprosium and erbium salts immediately follows the second stage, so that it is difficult to determine the temperature at which the second stage of dehydration of these salts ends and the third stage begins. At about 200 °C exothermic peaks are observed on the DTA curves. The temperatures at which the decomposition starts, the temperatures corresponding with the maxima of the peaks on the DTA and DTG curves, and the mass loss on the TG curve are all presented in Table 1. Figure 1 shows $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ thermal curves.

In the case of salts of the general formula $LnCl_3 \cdot 2HMTA \cdot 10H_2O$, one stage of dehydration is observed on the TG curve of the lanthanum salt. One peak (95 °C) occurs on the DTG curve, and one corresponding endothermic peak (92 °C) is present on the DTA curve. At 210 °C a weakly marked exothermic peak is observed on the DTA curve (Fig. 2a).

For praseodymium and neodymium salts in the temperature range 30–60 °C a peak of small intensity occurs on the TG curve, corresponding to the process of removing hygroscopic water. The two peaks on the DTG curve, at 85° and 175° for praseodymium and 87° and 107° for the neodymium salt, and on the DTA curve at 87° and 177° for praseodymium and 90° and 110° for the neodymium salt, indicate that dehydration of these salts is a two-stage process (Table 2).

TABLE 2

Data from the thermal curves of the salts of general formula $LnCl_3 \cdot 2HMTA \cdot 10H_2O$ and $LnCl_3 \cdot 2HMTA \cdot 8H_2O$ (Ln = La, Pr, Nd)

| Compound | DTG peak temp. (°C) | DTA peak temp. (°C) | Peak | Mass loss on the TG curve (%) |
|---|---|---|---|---|
| $LaCl_3 \cdot 2HMTA \cdot 10H_2O$ | 90 | 92 | Endothermic | 26.5 |
| | | 205 | Exothermic | – |
| $PrCl_3 \cdot 2HMTA \cdot 10H_2O$ | 85 | 88 | Endothermic | 12.5 |
| | 175 | 178 | Endothermic | 21.8 |
| $NdCl_3 \cdot 2HMTA \cdot 10H_2O$ | 85 | 90 | Endothermic | 15.5 |
| | 105 | 110 | Endothermic | 23.2 |
| | | 210 | Exothermic | – |
| $LaCl_3 \cdot 2HMTA \cdot 8H_2O$ | 80 | 82 | Endothermic | 12.8 |
| | 180 | 185 | Endothermic | 22.5 |
| | | 205 | Exothermic | – |
| $PrCl_3 \cdot 2HMTA \cdot 8H_2O$ | 80 | 82 | Endothermic | 12.6 |
| | 175 | 180 | Endothermic | 21.5 |
| | | 205 | Exothermic | – |
| $NdCl_3 \cdot 2HMTA \cdot 8H_2O$ | 50 | 50 | Endothermic | 6.0 |
| | 145 | 145 | Endothermic | 20.0 |
| | | 202 | Exothermic | – |

The thermal curves of the salts of general formula $LnCl_3 \cdot 2HMTA \cdot 8H_2O$ indicate the existence of two stages in their dehydration: there are two peaks on the DTG curves with corresponding endothermic peaks on the DTA curves and a distinct loss in means on the TG curves for each of the salts. At about 200 °C an exothermic peak occurs on each of the DTA curves (Table 2). Figure 2b presents $LaCl_3 \cdot 2HMTA \cdot 8H_2O$ thermal curves.

Figure 3 presents thermal curves of $NaCl_3 \cdot 2HMTA \cdot 12H_2O$ in the temperature range 20–1000 °C, obtained at a heating rate of 5° $min^{-1}$, TG sensitivity 100 and weighted sample mass 100 mg. The figure shows that as the salt is heated at temperatures above 200 °C, further mass loss occurs (TG curve) connected with the decomposition of the salt. The solid products of decomposition of $NdCl_3 \cdot 2HMTA \cdot 12H_2O$ obtained at 450 °C and at 900 °C were analyzed. The results of the determination of neodymium and chlorides confirm the presence of NdOCl [2] at 450 °C and of $Nd_2O_3$ at 900 °C. Volatile products of decomposition have not been analyzed.

## Chemical analysis of sinters

The salts were heated in a drier at a rate of 2.5° $min^{-1}$ at temperatures determined on the basis of the thermal curves. Mass losses were determined

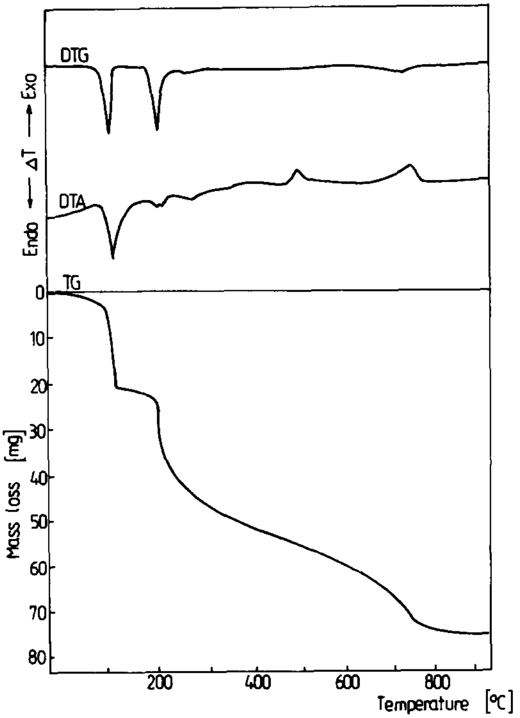

Fig. 3. Thermal analysis of $NdCl_3 \cdot 2HMTA \cdot 12H_2O$.

TABLE 3

Results of determination of thermal dehydration reaction products of $LnCl_3 \cdot 2HMTA \cdot 12H_2O$ (Ln = La, Pr, Nd)

| Compound | Stage of reaction | Determined |  |  | Calculated |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Ln (%) | Cl (%) | Mass loss (%) | Ln (%) | Cl (%) | Mass loss (%) |
| $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ | I | 23.89 | 18.45 | 22.3 | 23.98 | 18.36 | 21.8 |
| $LaCl_3 \cdot 2HMTA \cdot 3H_2O$ | II | 26.59 | 20.41 | 29.8 | 26.44 | 20.25 | 29.1 |
| $LaCl_3 \cdot 2HMTA$ |  |  |  |  |  |  |  |
| $PrCl_3 \cdot 2HMTA \cdot 12H_2O$ | I | 20.85 | 15.82 | 10.0 | 20.99 | 15.84 | 9.6 |
| $PrCl_3 \cdot 2HMTA \cdot 8H_2O$ | II | 25.18 | 18.97 | 24.9 | 25.01 | 18.88 | 24.2 |
| $PrCl_3 \cdot 2HMTA \cdot 2H_2O$ | III | 26.84 | 20.26 | 30.1 | 26.73 | 20.17 | 29.0 |
| $PrCl_3 \cdot 2HMTA$ |  |  |  |  |  |  |  |
| $NdCl_3 \cdot 2HMTA \cdot 12H_2O$ | I | 20.97 | 15.46 | 8.5 | 20.82 | 15.35 | 7.2 |
| $NdCl_3 \cdot 2HMTA \cdot 9H_2O$ | II | 25.76 | 18.87 | 25.7 | 25.46 | 18.77 | 24.1 |
| $NdCl_3 \cdot 2HMTA \cdot 2H_2O$ | III | 27.25 | 20.16 | 30.0 | 27.19 | 20.05 | 28.9 |
| $NdCl_3 \cdot 2HMTA$ |  |  |  |  |  |  |  |

TABLE 4

Results of determination of thermal dehydration reaction products of $LnCl_3 \cdot 2HMTA \cdot 10H_2O$ and $LnCl_3 \cdot 2HMTA \cdot 8H_2O$ (Ln = La, Pr, Nd)

| Compound | Stage of reaction | Determined | | | Calculated | | |
|---|---|---|---|---|---|---|---|
| | | Ln (%) | Cl (%) | Mass loss (%) | Ln (%) | Cl (%) | Mass loss (%) |
| $LaCl_3 \cdot 2HMTA \cdot 10H_2O$<br>$LaCl_3 \cdot 2HMTA$ | I | 26.53 | 20.37 | 26.7 | 26.44 | 20.24 | 25.5 |
| $PrCl_3 \cdot 2HMTA \cdot 10H_2O$<br>$PrCl_3 \cdot 2HMTA \cdot 5H_2O$<br>$PrCl_3 \cdot 2HMTA \cdot 1.5H_2O$ | I<br>II | 22.98<br>25.49 | 17.26<br>19.30 | 13.0<br>22.3 | 22.82<br>25.42 | 17.23<br>19.19 | 12.7<br>21.6 |
| $NdCl_3 \cdot 2HMTA \cdot 10H_2O$<br>$NdCl_3 \cdot 2HMTA \cdot 3H_2O$<br>$NdCl_3 \cdot 2HMTA \cdot H_2O$ | I<br>II | 24.00<br>26.38 | 17.86<br>19.48 | 15.8<br>23.0 | 23.93<br>26.29 | 17.65<br>19.38 | 15.1<br>22.8 |
| $LaCl_3 \cdot 2HMTA \cdot 8H_2O$<br>$LaCl_3 \cdot 2HMTA \cdot 3H_2O$<br>$LaCl_3 \cdot 2HMTA$ | I<br>II | 24.17<br>26.82 | 18.54<br>20.71 | 13.8<br>22.7 | 23.98<br>26.44 | 18.36<br>20.24 | 13.4<br>21.5 |
| $PrCl_3 \cdot 2HMTA \cdot 8H_2O$<br>$PrCl_3 \cdot 2HMTA \cdot 2H_2O$<br>$PrCl_3 \cdot 2HMTA$ | I<br>II | 24.09<br>26.51 | 18.04<br>20.28 | 13.1<br>22.5 | 24.24<br>26.72 | 18.29<br>20.17 | 13<br>21.4 |
| $NdCl_3 \cdot 2HMTA \cdot 8H_2O$<br>$NdCl_3 \cdot 2HMTA \cdot 6H_2O$<br>$NdCl_3 \cdot 2HMTA \cdot \frac{1}{2}H_2O$ | I<br>II | 22.63<br>26.84 | 16.80<br>19.88 | 5.7<br>19.6 | 22.59<br>26.73 | 16.65<br>19.71 | 5.3<br>20.0 |

TABLE 5

Activation energy $E_a$ and order $n$ of dehydration reactions determined for a selection of the examined salts

| Complex salt | Horowitz method | | Coats–Redfern method | |
|---|---|---|---|---|
| | Reaction order | $E_a$ (kJ mol$^{-1}$) | Reaction order | $E_a$ (kJ mol$^{-1}$) |
| $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ | 0.60 | 125 | 0.6 | 132 |
| $PrCl_3 \cdot 2HMTA \cdot 12H_2O$ | 0.10 | 58 | 0.1 | 63 |
| $NdCl_3 \cdot 2HMTA \cdot 12H_2O$ | 0.07 | 43 | 0.1 | 41 |
| $LaCl_3 \cdot 2HMTA \cdot 10H_2O$ | 0.14 | 102 | 0.2 | 110 |
| $PrCl_3 \cdot 2HMTA \cdot 10H_2O$ | 0.26 | 59 | 0.3 | 66 |
| $NdCl_3 \cdot 2HMTA \cdot 10H_2O$ | 0.50 | 72 | 0.5 | 79 |
| $LaCl_3 \cdot 2HMTA \cdot 8H_2O$ | 0.28 | 78 | 0.3 | 83 |
| $PrCl_3 \cdot 2HMTA \cdot 8H_2O$ | 0.21 | 91 | 0.2 | 96 |
| $NdCl_3 \cdot 2HMTA \cdot 8H_2O$ | 0.10 | 48 | 0.1 | 54 |

for individual salts, and the compounds formed as a result of decomposition were analyzed. Weighed samples of about 0.1 g of the salts were dissolved in a small amount of water acidified with $HNO_3$, and then $Cl^-$ and lanthanides were determined as in the case of the initial salts. The analysis data are presented in Tables 3 and 4.

### *Kinetic parameters*

The order of reaction $n$ and activation energy $E_a$ were calculated for the first stage of the thermal dehydration reaction of salts $LnCl_3 \cdot 2HMTA \cdot nH_2O$ where Ln = La, Pr, Nd and $n = 8, 10, 12$. The calculations were made by methods of Horowitz–Metzger [3] and Coats–Redfern [4]. The results of the calculated kinetic parameters are presented in Table 5.

## DISCUSSION AND CONCLUSIONS

As a result of the thermal decomposition—the dehydration reaction—salts of intermediate hydration state and anhydrous salts were obtained. Anhydrous salts were obtained as a result of the dehydration of 12-hydrous La, Pr, Nd, Gd, Dy and Er salts and of 10- and 8-hydrous lanthanum salts. On the basis of the obtained results of the decomposition products analysis, the following dehydration reactions were suggested

$$LaCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{65\,^{\circ}C} LaCl_3 \cdot 2HMTA \cdot 3H_2O \xrightarrow{130\,^{\circ}C} LaCl_3 \cdot 2HMTA$$

$$PrCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{50\,^{\circ}C} PrCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{85\,^{\circ}C} PrCl_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{135\,^{\circ}C} PrCl_3 \cdot 2HMTA$$

$$NdCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{60\,^{\circ}C} NdCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{90\,^{\circ}C} NdCl_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{100\,^{\circ}C} NdCl_3 \cdot 2HMTA$$

$$GdCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{65^{\circ}} GdCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{100\,^{\circ}C} GdCl_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{140\,^{\circ}C} GdCl_3 \cdot 2HMTA$$

$$DyCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{60\,^{\circ}C} DyCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{105\,^{\circ}C} DyCl_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{140\,^{\circ}C} DyCl_3 \cdot 2HMTA$$

$$ErCl_3 \cdot 2HMTA \cdot 12H_2O \xrightarrow{60\,^{\circ}C} ErCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{100\,^{\circ}C} ErCl_3 \cdot 2HMTA \cdot 2H_2O \xrightarrow{135\,^{\circ}C} ErCl_3 \cdot 2HMTA$$

$$LaCl_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{90\,^\circ C} LaCl_3 \cdot 2HMTA$$

$$PrCl_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{85\,^\circ C} PrCl_3 \cdot 2HMTA \cdot 5H_2O$$

$$\xrightarrow{175\,^\circ C} PrCl_3 \cdot 2HMTA \cdot 1.5H_2O$$

$$NdCl_3 \cdot 2HMTA \cdot 10H_2O \xrightarrow{85\,^\circ C} NdCl_3 \cdot 2HMTA \cdot 3H_2O$$

$$\xrightarrow{105\,^\circ C} NdCl_3 \cdot 2HMTA \cdot H_2O$$

$$LaCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{80\,^\circ C} LaCl_3 \cdot 2HMTA \cdot 3H_2O$$

$$\xrightarrow{180\,^\circ C} LaCl_3 \cdot 2HMTA$$

$$PrCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{80\,^\circ C} PrCl_3 \cdot 2HMTA \cdot 2H_2O$$

$$\xrightarrow{175\,^\circ C} PrCl_3 \cdot 2HMTA$$

$$NdCl_3 \cdot 2HMTA \cdot 8H_2O \xrightarrow{50\,^\circ C} NdCl_3 \cdot 2HMTA \cdot 6H_2O$$

$$\xrightarrow{145\,^\circ C} NdCl_3 \cdot 2HMTA \cdot 0.5H_2O$$

Processes of thermal dehydration of the obtained salts take a few stages and the change of hydration state is accompanied by a change of coordination sphere composition and space group symmetry [1].

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