

COMPLEX THERMOANALYTICAL STUDIES ON VOLATILE RARE EARTH ELEMENT β -DIKETONATES

T. N. Martynova, L. D. Nikulina and V. A. Logvinenko

INSTITUTE OF INORGANIC CHEMISTRY, NOVOSIBIRSK, 630090, USSR

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Experimental data on the thermal characteristics of β -diketonates of rare earth elements (REE) are discussed. Tris chelates $\text{LnL}_3 \cdot n\text{H}_2\text{O}$ and tetrakis chelates $\text{Na}[\text{LnL}_4]$ (L = different β -diketones) are considered. The volatility and thermal stability of these β -diketonates depend on several factors, e.g. the hydrate composition and the organic substituents in the ligand. Hydrolysis is possible during the dehydration of light REE tris chelates. Increase volatility and thermal stability are maintained by the introduction of sterically hindered and fluorinated substituents onto the chelate ring of the complex.

It is known that β -diketonates containing branched and fluorinated substituents readily form volatile complexes with salts of the rare earth elements (REE). Owing to these properties, they are widely used in the separation of the REE by means of the fractional sublimation technique [1], and such REE complexes are also used in some fields of microelectronics [2, 3]. In this connection, the most typical problems in studies of their physical and chemical properties are the thermal stability and volatility. The data from the literature are incomplete [4, 5], which was the reason for this paper, which combines the results of earlier published articles [6-8] and new results.

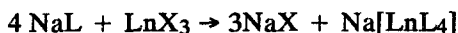
The following materials were studied: REE tris chelates, with common formula $\text{LnL}_3 \cdot n\text{H}_2\text{O}$, where Ln stands for any REE, L = trifluoroacetylacetone (TFA), hexafluoroacetylacetone (HFA), pivaloyltrifluoroacetone (PTA), dimethylheptafluoroacetonedione (FOD) and dipivaloylmethane (DPM); and REE tetrakis chelates, containing an alkali metal cation, with common formula $\text{Na}[\text{LnL}_4]$.

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Experimental

The complexes $\text{LnL}_3 \cdot n\text{H}_2\text{O}$ were obtained by the reaction of the β -diketone with the REE salt under neutral homogeneous (water-alcohol) or heterogeneous (water-chloroform) conditions [6]. The substances were dried by keeping them in vacuum over P_2O_5 . The water content in the tris chelates was determined by the Fischer method. It was found that complete dehydration of the complexes does not occur under drying, since the substances contain trace quantities of water ($n = 0.2-1$).

Tetrakis chelates, containing an alkali metal ion, were obtained in slightly polar solvents at the boiling temperature of the reaction mixture [7], according to the following scheme:



where $X = \text{Cl}^-$, NO_3^- or CH_3OCO^- .

This results in complexes which are anhydrous and nonhygroscopic.

Thermoanalytical studies were conducted with a derivatograph (MOM, Hungary) in a helium flow. The sample mass was 40-80 mg; sample holder: ceramic crucible; heating rate 5 deg/min or 10 deg/min; TG 50 mg and 100 mg.

In order to be able to compare the data, the TG studies were in some case conducted with a Setaram thermoanalyser with a symmetric oven in a following inert atmosphere, at a heating rate of 5 deg/min. High-purity helium was used as the inert atmosphere, at a flow rate of 10-100 cm^3/min . The sample mass was 8-10 mg.

Results and discussion

The most interesting complexes $\text{Ln}(\text{PTA})_3$ are those with asymmetric ligands, which successively combine the tert-butyl group, weakening intermolecular contacts, and the trifluoromethyl group, providing the stability for sublimation.

The DTA curves of the complexes studied in the La-Lu series exhibit the common regularity. They contain distinctly expressed endoeffects not accompanied by mass loss and corresponding to the phase transition (melting); after this, a considerable mass loss is observed due to evaporation.

Evaporation of most of the complexes occurs with partial decomposition in the temperature range 240-300°, which is confirmed by the presence of an intricate exoeffect and the mass loss character. The decomposition temperature increases to the end of the lanthanide series, and the compounds of Er, Dy and Lu evaporate practically completely without decomposition. These data provide evidence of the increasing thermal stability of tris chelates up to the end of the REE series.

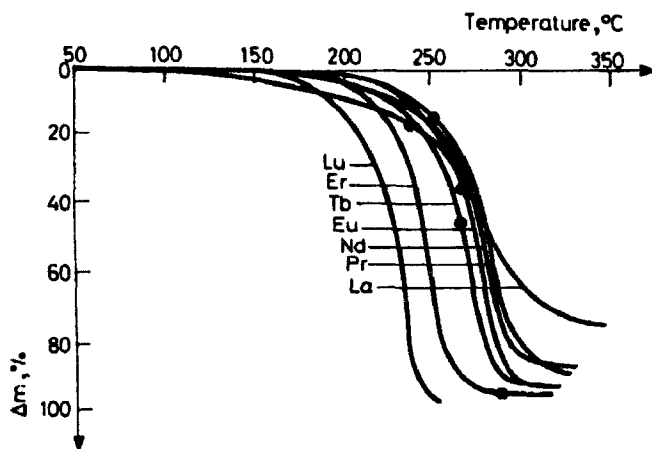


Fig. 1 TG curves of the complexes $\text{Ln}(\text{PTA})_3$ (dry),

On analogy, an increase in volatility is observed in the series La-Lu, despite the increase in molecular weight (Fig. 1). Such a phenomenon is known for the lanthanides [8]. This is usually explained by the decrease in the size of the chelate molecule with the metal ion radius (lanthanide compression). As a result, the intramolecular local dipoles either decrease in size, or are better screened from the intermolecular interaction forces.

It can be seen in Fig. 1 that all the complexes except $\text{La}(\text{PTA})_3$ sublime practically quantitatively leaving a negligible non-volatile residue. However, the sublimation process for the light lanthanide complexes is accompanied by partial decomposition in the temperature interval 240-300°. The volatility features of the lanthanide complexes are obviously related to the fact that attempts to dehydrate $\text{La}(\text{PTA})_3 \cdot 2\text{H}_2\text{O}$ did not give positive results. The study of the influence of the water content on the thermal properties of the

complexes revealed that the volatility and the thermal stability depend directly upon the hydration of the tris chelates (Table 1).

Table 1 Characteristics of thermal stability of the $\text{LnL}_3 \cdot n\text{H}_2\text{O}$

| Compound | Temperature, °C | | | H ₂ O, % according | | Non-volatile residue, % |
|---|-----------------|---------|---------|-------------------------------|-------|-------------------------|
| | dehydration | melting | decomp. | to Fischer | to TG | |
| La(PTA) ₃ | 70 | 136 | 239 | 1.5 | 1.78 | 15 |
| La(PTA) ₃ ·2H ₂ O | 69-73, 167 | 136 | 240 | 4.40 | 3.0 | 25 |
| Pr(PTA) ₃ | 73 | 132 | 252 | 0.40 | 0.54 | 6.6 |
| Eu(PTA) ₃ | 69 | 122 | 269 | 0.3 | 0.32 | 5.8 |
| Tb(PTA) ₃ | 60 | 145-147 | 264 | 0.60 | 0.80 | 7.9 |
| Tb(PTA) ₃ ·2H ₂ O | 60 | 64 | 260 | 4.50 | 4.20 | 10.7 |
| Nd(PTA) ₃ | 80 | 149 | 264 | 0.80 | 1.0 | 10.5 |
| Nd(PTA) ₃ ·H ₂ O | 125 | 149 | 276 | 2.50 | 2.67 | 10.4 |
| Nd(PTA) ₃ ·2H ₂ O | 80-149 | 80, 149 | 257 | 4.60 | 4.0 | 11.5 |
| Er(PTA) ₃ | | 156 | | | | 3.3 |
| Er(PTA) ₃ ·H ₂ O | 111 | 144 | | 2.30 | 2.41 | 4.0 |
| Lu(PTA) ₃ ·2H ₂ O | 117 | 178 | | 2.30 | 2.48 | 2.1 |
| Nd(PTA) ₃ ·2H ₂ O | 80, 110 | | 210 | 5.68 | 3.9 | 35 |
| Nd(GFA) ₃ ·3H ₂ O | 80, 110, 150 | | | 6.8 | 7.0 | 8 |
| Nd(DPM) ₃ | | 220 | | | | 4 |

Comparative TG and DTA curves of neodymium complexes with various water contents (Fig. 2) show that dried Nd(PTA)₃ loses trace quantities of water at 80 °, then melts at 149° and evaporates to leave an insignificant non-volatile residue. The intricate exoeffect in the DTA curve is related to the decomposition of the non-volatile residue. The monohydrate Nd(PTA)₃·H₂O undergoes dehydration, losing one water molecule at higher temperature (125°), with an endoeffect in the DTA curve. The second endoeffect, at 149°, which occurs without mass loss, may be related to the melting. The product then evaporates to leave a negligible non-volatile residue, which decomposes in approximately the same temperature range as the dried complex. In Fig. 2 it can be seen that the dehydration of the substance is a divariant process; by visual determination of the melting temperature on a Kofler block, it was found that the first endoeffect (observed at 80°) is to be attributed to incongruent melting of the complex in its crystallization water. Here, the substance partially melts, forming a new solid phase (lower hydrate) and saturated solution; further water loss is related to dehydration of the monohydrate. Practically complete dehydration takes place at 149°. At the same temperature the tris chelate melts. The endoeffect at 172 ° can be explained by hydrolysis with the release of gaseous

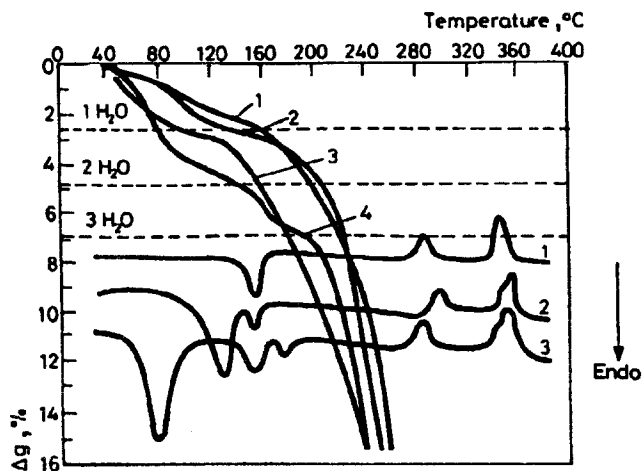


Fig.2 TG and DTA curves for tris-chelates of light REE

product and the formation of a new phase, which then decomposes at 257°. Hydrolytic splitting of the tris chelates can be represented by the following scheme:



The newly formed hydroxo complexes are thermally unstable and readily polymerize, liberating gaseous product and leaving a high percentage of non-volatile residue. The most inclined to hydrolytic splitting are $\text{Nd(TFA)}_3 \cdot 2\text{H}_2\text{O}$ and $\text{La(PTA)}_3 \cdot 2\text{H}_2\text{O}$. Thermoanalytical curves of $\text{La(PTA)}_3 \cdot 2\text{H}_2\text{O}$ are given in Fig. 3. The DTA curve shows that complete dehydration of the product does not occur; a constant mass loss, however, is observed up to the evaporation temperature. Three endoeffects are observed at 70°, 136° and 167°; the non-volatile residue accounts for 25%.

Heavy REE tris chelates (Er, Yb, Lu) are completely dehydrated when heated in the inert atmosphere, and then behave similarly to the anhydrous complexes. During this process, they evaporate completely when heated, and do not undergo self-hydrolysis. These complexes are thermally stable up to 300°, as confirmed by the lack of exoeffects in the DTA curve (Fig. 3).

It is known that the presence of coordination water in the compound causes the melting temperature to decrease [4]. This regularity is preserved in the $\text{Ln}(\text{PTA})_3 \cdot n\text{H}_2\text{O}$ series; the temperature decrease is less for monohydrates than for dihydrates (Table 1). The dehydration of monohydrates also starts at higher temperature. This is possibly related to the fact that the water in them is in the lanthanide inner coordination sphere, and is more firmly bonded.

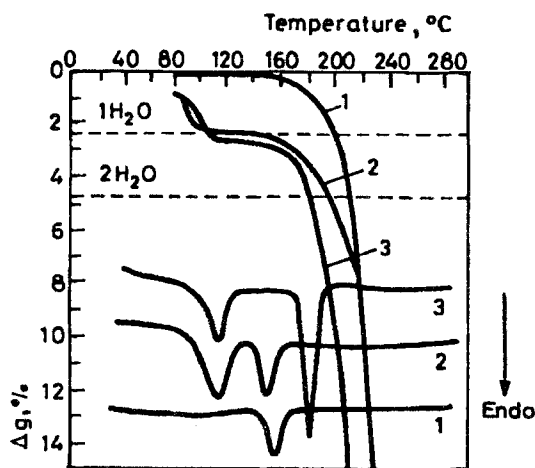
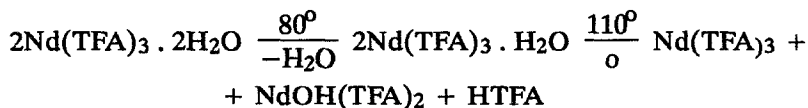


Fig.3 TG and DTA curves for tris-chelates of heavy REE

The dehydration of dihydrates has two stages. The outer sphere molecule of coordination water is split off at higher temperatures. However, the second endoeffect is indistinct since the melting effect is imposed. Another complex series with inhomogeneous substituents in the chelate ring are $\text{Ln}(\text{TFA})_3$. However, substitution of the tert-butyl group for the methyl group in the HPTA ligand results in a considerable decrease in thermal stability of the complexes. Thus, $\text{Nd}(\text{TFA})_3 \cdot 2\text{H}_2\text{O}$ behaves as follows when heated. Two effects are observed relating to dehydration, at 80° and 110° . In the first case, one molecule of outer sphere water is split off; in the second, the mass loss corresponds to incomplete dehydration of the complex (70%), which can be explained by the following reaction:



The hydroxo complex obtained is thermally unstable, and the sublimation is accompanied by the destruction of this substance: the presence of two exoeffects within the temperature range between 210° and 242° and the considerable percentage of the non-volatile residue (35%) confirm this. The maximum sublimation temperature here is 235°.

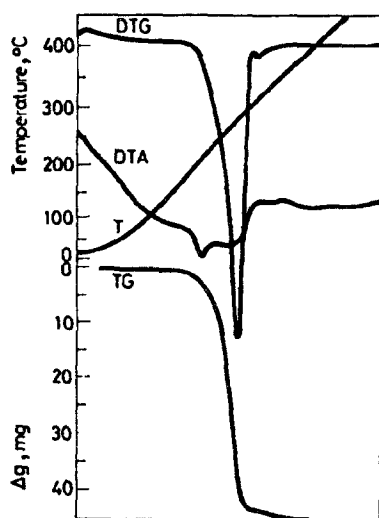


Fig.4 DTA-TG-DTG curves of Nd dipivaloylmethane

The completely fluorinated substituents considerably improve the thermal stability of the complexes $\text{Ln}(\text{HFA})_3$. Let us consider the complex $\text{Nd}(\text{HFA})_3 \cdot 3\text{H}_2\text{O}$ for the sake of comparison. Its dehydration occurs completely within the range 80-150°, in two stages, which is confirmed by the presence of three endoeffects in the DTA curve (80, 100 and 150°). The largest mass loss is observed at 150°. The substance then sublimes, the maximum temperature being 245°, and the non-volatile residue is 8%.

The highest thermal stability is exhibited by the complexes with two tert-butyl substituents. In the synthesis they are obtained practically anhydrous;

the water content is 0.5 mole per mole of complex. Water, however, is easily split off when they are heated in vacuum. Thus, in the DTA curve of the complex $\text{Nd}(\text{DPM})_3$ a melting endoeffect is observed at 220° , with subsequent sublimation ($T_{\text{max}} = 280^\circ$), and the non-volatile residue is only 4%. There is a considerable decrease in volatility of the DPM complex as compared to their fluorinated analogues (Fig. 4).

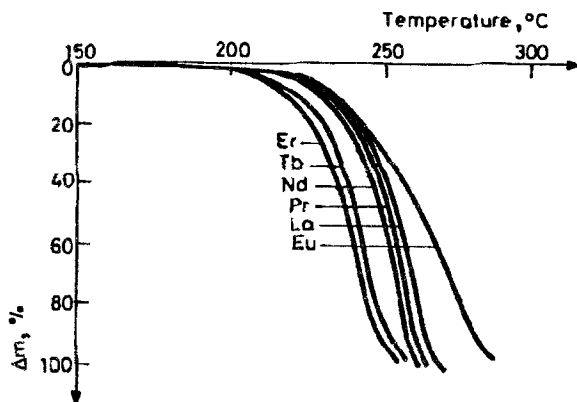


Fig.5 TG curves of Ln tetrakis(pivaloyl)trifluoroacetates

It is seen from the above studies, that the presence of water in the complexes of tris chelates decreases their thermal stability essentially, and sublimation is not always productive. There are simpler techniques of substitution of water by additional ligands. One such opportunity is shown by the example of the synthesis of tetrakis chelates containing an alkali metal ion e.g. $\text{Na}[\text{Ln}(\text{PTA})_4]$, which appears to be anhydrous and non-hygroscopic [7]. Study of these substances showed that in an inert atmosphere they sublime without decomposition within the temperature range $150\text{--}300^\circ$. This is confirmed by the absence of exoeffects in the DTA curve. Analysis of the TG curves shows that the volatility of the complexes $\text{Na}[\text{Ln}(\text{PTA})_4]$ increases to the end of the REE series (Fig. 5).

The studies on the tetrakis chelates revealed the presence of melting endoeffects within the range $240\text{--}270^\circ$, depending on the REE character, and the melting temperature normally decreases to the end of the lanthanide series. The presence of the second endoeffect, related to the polymorphous transformation of the substances, was found for the derivatives of La, Eu and Er (Table 2).

Table 2 Thermoanalytical data of tetrakis-chelates

| Compound | Temperature, °C | | | Non-volatile residue, % |
|---------------------------|-----------------------|--|-----------------|-------------------------|
| | Melting $\pm 3^\circ$ | polymorphous transformations $\pm 3^\circ$ | Decomp. (refer) | |
| Na[La(PTA) ₄] | 267 | 258 | 252-256(9) | |
| Na[Pr(PTA) ₄] | 269 | | | |
| Na[Nd(PTA) ₄] | 267 | | 254-256(9) | |
| Na[Eu(PTA) ₄] | 240 | 225 | 245-257(9) | |
| Na[Tb(PTA) ₄] | 240 | | 237-240(9) | |
| Na[Er(PTA) ₄] | 241 | 212 | | |
| Na[La(TFA) ₄] | 220-270 (volat.) | | 290 | 13 |
| Na[Nd(TFA) ₄] | 250-280 | | 295 | 33 |
| Na[Tb(TFA) ₄] | 215-290 | | 300 | 16 |
| Na[Er(TFA) ₄] | 230-295 | | | 35 |

It should be noted that [9] gives not the melting temperatures of the substances, but their decomposition temperatures. However, as already specified, our studies did not record the effects of decomposition, and the destruction of the tris chelates proceeds in an approximately similar temperature range. Obviously, this can be explained by the compounds studied in [9]. Eventually, in the DTA curve of the poorly purified complex Na[Eu(PTA)₄] we recorded two exoeffects at 269° and 307°, coinciding with those for the tris chelates (Fig. 5). After additional purification, there are no such effects in the DTA curve, and the substance sublimes almost completely.

A comparison of the TG curves of tris and tetrakis chelates obtained under similar conditions indicates the higher volatility and the thermal stability of the latter. This contradicts the supposition that anhydrous tris chelates should be more volatile.

Tetrakis chelates of HTFA with REE, Na[Ln(TFA)₄] sublime within the range 215-295°; however, in contrast with Na[Ln(PTA)₄] the compounds obtained partially decompose in the process of sublimation. This is confirmed by the presence of, a distinct exoeffect in the DTA curve when $T_{\text{exo}} > T_{\text{subl}}$. The large percentage of non-volatile residue (33%) shows that within the temperature range under study (290-310°) the transformation of the substance takes place. The presence of the exoeffect can be explained either by a polymorphous transformation, or by intramolecular oxidation.

The complex thermal analysis data given in Table 2 show that the thermal stability of the tris chelates improves up to end of the lanthanide series. A

more essential increase in volatility is observed with a higher percentage of fluorine in the molecule.

Thus, $\text{Na}[\text{Nd}(\text{FOD})_4]$ sublimes almost completely within the range 135-270°, the temperature of the maximum process rate being 250°. The absence of a non-volatile residue and of exoeffects in the DTA curve is evidence of the high thermostability of these compounds within the above temperature range.

Thus, this work has shown that the volatility and thermal stability of the REE tris chelates depend upon several factors; the hydrate composition, REE character, and organic substituents in the ligand. When heated, the hydrated complex of the light REE (La-Nd) are not completely dehydrated, and undergo self-hydrolysis with the formation of thermally unstable hydroxo complexes. By the end of the REE series (Er-Yb), practically complete dehydration is observed, with the formation of anhydrous volatile tris chelates. The introduction of sterically hindered and fluorinated substituents onto the chelate ring of the complexes results in weakening of the intermolecular contacts and, as a consequence, in improvements in volatility and thermal stability.

Coordination-saturated octacoordinated complexes (tetrakis chelates) behave in a similar manner, but have higher thermal stability and volatility than the tris chelates. Within the series of these compounds, the same normal dependences are observed on the organic substituent of the ligand: $\text{Na}[\text{Ln}(\text{TFA})_4] < \text{Na}[\text{Ln}(\text{PTA})_4] < \text{Na}[\text{Ln}(\text{FOD})_4]$.

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Zusammenfassung -Es werden experimentelle Daten zur themischen Charakterisierung von β -Diketonaten von Seltenerdenelementen (SEE) besprochen. Dabei wurden Tris-chelate $\text{LnL}_3 \cdot n\text{H}_2\text{O}$ und Tetrakis-chelate $\text{Na}[\text{LnL}_4]$ mit verschiedenen β -Diketonen als L betrachtet.

Flüchtigkeit und thermische Stabilität dieser β -Diketonate hängen von verschiedenen Faktoren ab, z.B. von der Hydratzusammensetzung und der Art der organischen Substituenten der Liganden. Während der Dehydratation der Tris-chelate von leichten SEE ist Hydrolyse möglich. Erhöhte Flüchtigkeit und thermische Stabilität werden durch Einbau von sterisch behinderten und fluorierten Substituenten in den Chelatring aufrechterhalten.