

SOLID STATE DECOMPOSITION STUDIES ON METAL SALICYLATES. THERMAL DECOMPOSITION OF DYSPROSIUM SALICYLATO COMPLEXES

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ABSTRACT

Dysprosium(III) salicylate di- and pentahydrate complexes were prepared and characterized by elemental analyses and IR spectra. The mechanisms of thermal decomposition of these complexes were studied using TG, DTG and DSC techniques. The TG curves show three main steps of decomposition. The solid intermediates formed at the different decomposition stages were isolated and analyzed by IR and mass spectrometry. For both of the complexes the first two steps are endothermic, while the third step before Dy₂O₃ oxide formation is strongly exothermic.

INTRODUCTION

Although the research on the rare earth compounds has notably increased during recent years, there are only a few papers concerning the thermal behaviour of lanthanide complexes, especially ones formed with organic ligands [1–6]. With only a few exceptions organolanthanides presented in the literature are concerned only with the trivalent state [7]. The lanthanides exhibit great similarities in many of their physical properties, and it is mainly only when the 4 *f*-electrons are directly involved that they show distinctly different behaviour. In our laboratory, complex formation of the *d*-block elements with unsubstituted and 5-substituted salicyclic acids both in liquid and solid phases has been widely studied [8–11]. In order to compare the complex formation and thermal behaviour of the lanthanide salicylates with each other and the lanthanide complexes with the corresponding transition metal complexes, we initiated this new series of investigations. Firstly, we studied the mechanism and thermal behaviour of dysprosium(III) salicylato di- and pentahydrates. Because of the relatively detailed representation, we limited this paper to cover only the dysprosium salicylate complexes.

EXPERIMENTAL

Reagents

The dysprosium oxide (Dy_2O_3 , 99.9%) was obtained from Fluka AG. The salicylic acid (H_2sal , extra pure grade) was supplied by Merck.

Preparation of the dysprosium salicylate hydrates

The dysprosium sulphate hydrate, $\text{Dy}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$, was prepared as described previously [12]. 5 ml of 0.15 M $\text{Dy}_2(\text{SO}_4)_3$ solution and 5 ml of 1 M sodium salicylate solution whose pH was adjusted to 6.5 by NaOH were mixed. The pH of the resulting solution was adjusted to 5.36 and 5.50 using dilute NaOH and H_2SO_4 solutions. From the solution with pH 5.36, white $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ crystals were precipitated at room temperature over a period of 1 h. In the case of the second solution (pH 5.50) the precipitation of white $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ crystals took 6 days at room temperature under the cover of a thin parafilm. After filtration the crystals were washed twice with 20 ml of water and once with 20 ml of 95% ethanol. The products were filtered off and dried in a vacuum desiccator at room temperature. The analytical data of the complexes are given in Table 1.

Instrumental

TG runs were carried out on a Mettler TG 50 thermobalance in a temperature range 293–1023 K. The sample quantity varied between 9.4 and 9.8 mg. The dynamic runs were made in air at a flow rate of 200 ml min^{-1} and a heating rate of 5 K min^{-1} was used. ΔH measurements were performed on a Mettler DSC-20 differential scanning calorimeter between 298 and 873 K. The dynamic runs were carried out at a heating rate of 5 K min^{-1} under an air atmosphere (50 ml min^{-1}), using 5–6 mg samples. IR spectra were measured in a KBr matrix on a Perkin-Elmer 457 grating spectrometer in the range $250\text{--}4000 \text{ cm}^{-1}$. The mass spectra of the decomposition products were recorded at a scanning rate of 1 s/decade on a Kratos MS 80 RF mass spectrometer, using the direct inlet and heating the

TABLE 1

Analytical data

Compound	Dy (%)		H (%)	
	Calc.	Found	Calc.	Found
$\text{Dy}(\text{C}_7\text{H}_5\text{O}_3)_3 \cdot 2 \text{H}_2\text{O}$	26.6	25.7	3.1	3.1
$\text{Dy}(\text{C}_7\text{H}_5\text{O}_3)_3 \cdot 5 \text{H}_2\text{O}$	24.5		3.8	3.5

sample at a rate of 50 K min^{-1} . The metal contents of the compounds were determined with DCP-AES (Spectra Span III B) and the hydrogen contents with an element analyzer (Leco RH2). The analytical data of the compounds are given in Table 1.

RESULTS AND DISCUSSION

The TG, DTG and DSC curves given in Figs. 1 and 2 show that the thermal decomposition of the two dysprosium compounds takes place in two endothermic and one exothermic reaction steps. The first step in both cases is due to the dehydration. Table 1 shows that dysprosium salicylate dihydrate is thermally more stable than the corresponding pentahydrate. The anhydrous dysprosium salicylate complexes decompose upon heating at two successive stages. The weight losses correspond to a release of one and a half ligand acid molecules at both stages. The second decomposition step takes place within a narrow temperature range, while the peak corresponding to the third step is broad and divided into two parts. The latter phenomenon of peak splitting is also seen in the DSC curve (Fig. 2). In addition, a minor weight loss can be observed in Fig. 1 for the two compounds in the temperature range 793–1023 K before the formation of the stable Dy_2O_3 .

The reaction mechanism of the decomposition of dysprosium salicylate complexes was also studied by IR and mass spectrometry. The IR and mass spectra are shown in Figs. 3–6. The temperatures of 373, 558, 663 and 823 K refer to the intermediate products left after heating up to the given tempera-

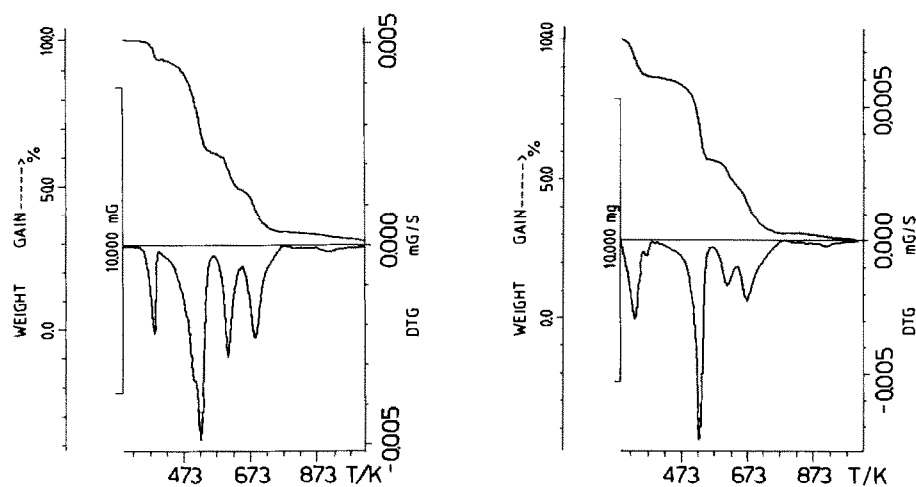


Fig. 1. TG curves of $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ (left) and $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ (right).

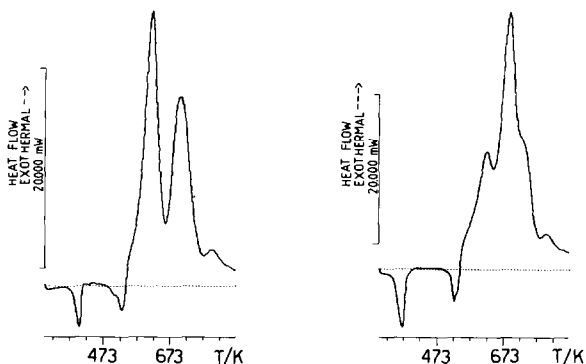


Fig. 2. DSC curves of $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ (left) and $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ (right).

ture. IR spectra were recorded in a KBr matrix and mass spectra obtained by heating these intermediate products using the direct inlet system.

The IR spectra of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ and $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ are very similar. The only discrepancies found are that the stretching $\nu(\text{O} \cdots \text{H})_{\text{H}_2\text{O}}$, $\nu(\text{O} \cdots \text{H})_{\text{ph}}$ and bending $\nu(\text{C}-\text{H}-\text{C})$ vibrations at 3600, 3200 and 1150 cm^{-1} , respectively are stronger for dihydrate than pentahydrate compounds. The IR spectra of dysprosium and transition metal salicylato complexes as a rule seem to deviate clearly from one another but in the case of the $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ and $\text{Zn}(\text{Hsal})_2 \cdot 2 \text{H}_2\text{O}$ they are very similar [9]. Their IR spectra deviate only at 475 cm^{-1} , where the $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ has a stretching vibration peak. The IR spectra of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ at the different temperatures show clearly that along with an increasing temperature, the frequencies due to organic compounds gradually disappear and the quality of an inorganic compound (Dy_2O_3) emerges. A significant observation on the IR spectra is that there is no evidence of stretching vibration of free ligand acid at any of the decomposition stages. Figure 4 shows the total ion chromatogram of pure $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$, and the

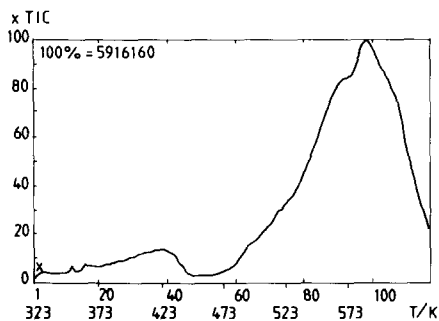


Fig. 3. Total ion chromatogram of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ as a function of scan numbers and temperature taken with the straight inlet system of the sample.

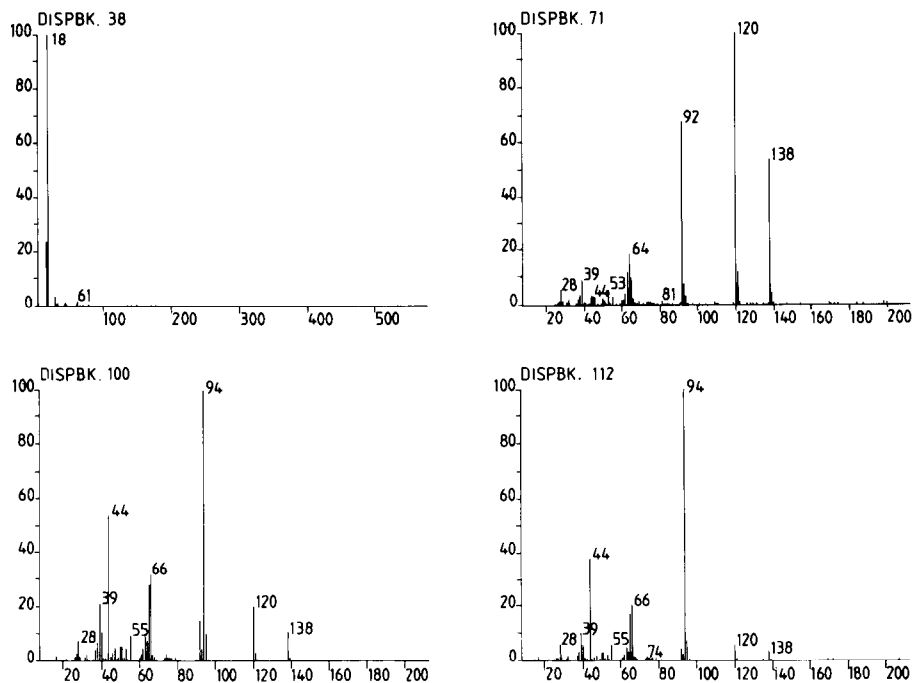


Fig. 4. Mass spectra of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ taken from the points of scan numbers 38, 71, 100 and 112 of the total ion chromatogram presented in Fig. 3

corresponding mass spectra are presented in Fig. 5. This same procedure was applied to the samples of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ preheated by TG up to temperatures of 373, 558, 663 and 823 K which are situated between the successive stages. We then analyzed these solid decomposition products by MS using the direct inlet system. The main fragments (m/z) found were 138, 120, 94, 92, 66, 64, 44, which refer to the fragments of the salicylic acid (138) and decarboxylation products of salicylic acid (phenol (94) and carbon dioxide (44)). These same fragments in the same form but at different intensity ratios also occurred at the other temperatures studied, with the exception of the complex heated to 823 K, which does not give any fragment by MS.

After this, therefore, we only studied the fragments 138, 94 and 92 (m/z) representing two different types of thermal decomposition process: (1) the ligand acid is released as free acid, or (2) decarboxylation of the ligand acid takes place. Figure 6 shows the influence of heating the complex on these two different types of decomposition processes. It can be clearly deduced from the TG that the decarboxylation process increases with increasing temperature of the complex. This means that during stage II the ligand acid decomposes mainly according to the decomposition type (1) while at stage III the main decomposition process is decarboxylation. This conclusion

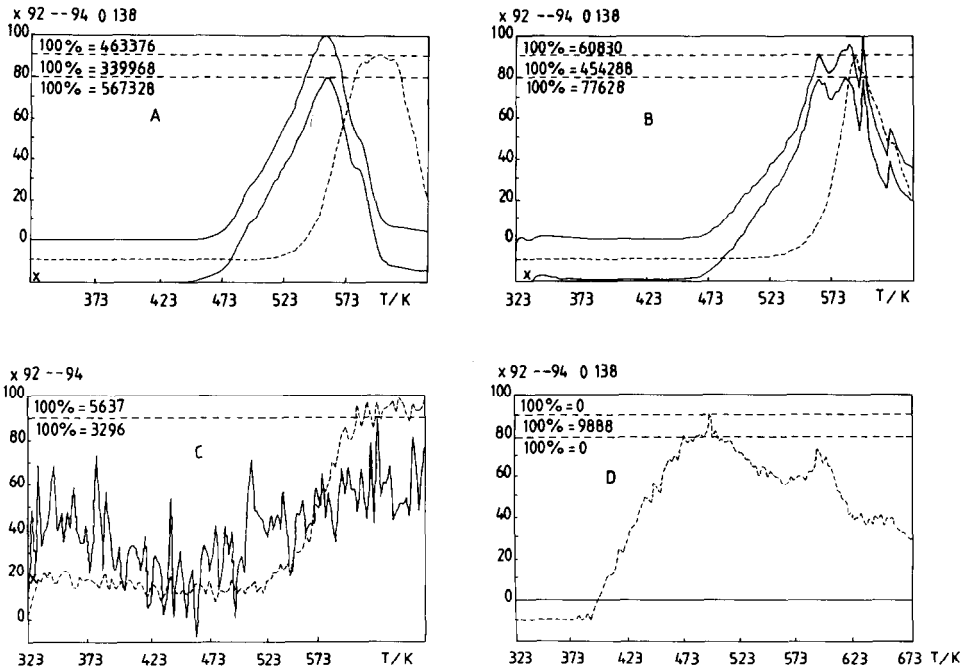


Fig. 5. Mass chromatograms of ions 92, 94 and 138 (m/z). The letters, A, B, C and D refer to the temperatures 298, 398, 558 and 663 K, respectively, the temperatures to which the $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ complexes were preheated before the MS analysis.

agrees with our earlier studies where we gathered the gaseous thermal decomposition products of the transition metal salicylato complexes from the desired temperature range, condensed them by the cold-finger technique and then analyzed them on a Kratos GC-MS spectrometer [8,13]. The final decomposition product, Dy_2O_3 , was confirmed by IR and DCP-AES spectroscopy.

The decomposition of the two complexes seems according to our studies (Table 2) to proceed as follows:

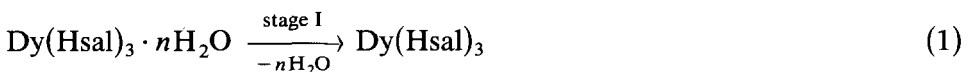


Table 3 shows that the ΔH values of both the endothermic and the exothermic decomposition stages of $\text{Dy}(\text{Hsal})_3$ complexes are clearly higher than the values for the transition metal salicylato complexes(II). Brzyska et al. [5] found that the loss of crystalline water is accompanied by a strong

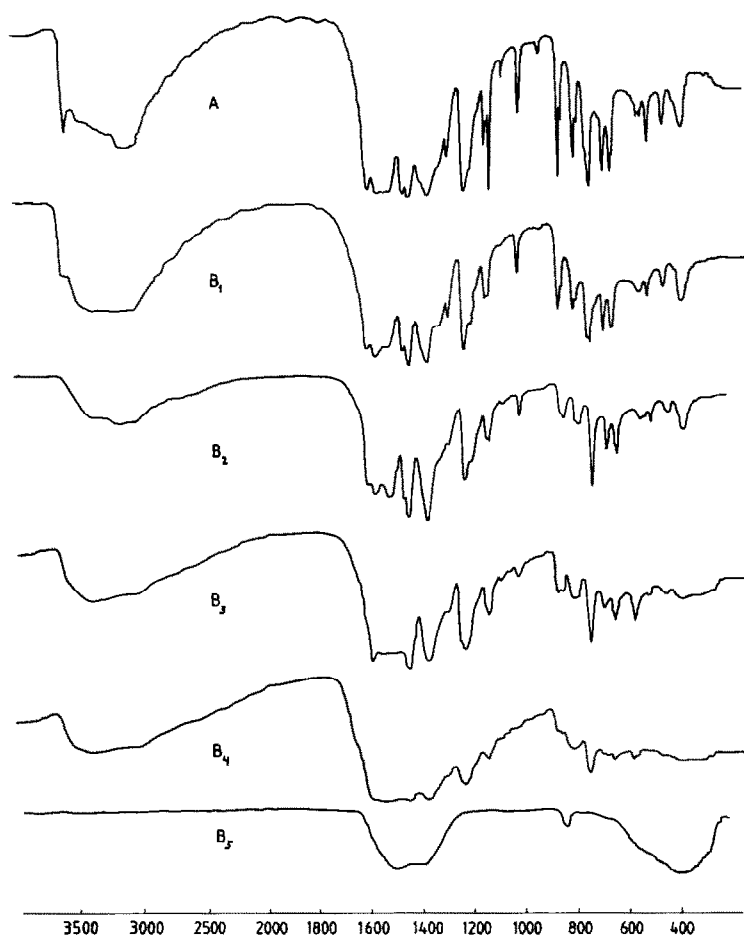


Fig. 6. IR spectra of $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ (A) and $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ (B). B_1 , B_2 , B_3 , B_4 and B_5 refer to the temperatures 298, 398, 558, 663 and 823 K, respectively, the temperatures to which the $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ complex was heated by TG before the IR analysis.

endothermic effect. Further, we observe (Fig. 2) that in the case of a di- or pentahydrated dysprosium salicylato complex that the exothermic peak attributed to the third decomposition stage has split into two peaks while the corresponding peak in the case of a transition metal (Cd, Cu, Mn, Ni and Zn) salicylato complex has no split. To explain these differences between the corresponding *d*-block and *f*-block element complexes, we need to know more about the structures of the compounds. On the basis of X-ray analysis data determined for *d*-block complexes [9] and in progress for *f*-block compounds, we will probably be able to interpret these differences.

In conclusion, we can say that the dehydration process of $\text{Dy}(\text{Hsal})_3 \cdot 5 \text{H}_2\text{O}$ and $\text{Dy}(\text{Hsal})_3 \cdot 2 \text{H}_2\text{O}$ compounds begins at low temperatures, and that this process requires more energy than the corresponding transition

TABLE 2

TG data on the decomposition of dysprosium salicylato complexes

Dy(Hsal) ₃ ·5 H ₂ O			Dy(Hsal) ₃ ·2 H ₂ O		
<i>T</i> range (K)	<i>T</i> _p (K)	Weight loss (%)	<i>T</i> range (K)	<i>T</i> _p (K)	Weight loss (%)
<i>Stage I</i>					
294–380	334	13.4	348–399	388	6.0
<i>Stage II</i>					
423–565	523	29.5	399–564	525	32.2
<i>Stage III</i>					
574–767	672	26.2	564–763	690	27.4
<i>Residual weight loss (%)</i>					
Calculated		28.1			30.6
Found		28.3			31.0

TABLE 3

Enthalpy changes, ΔH , for the decomposition of the complexes

Dy(Hsal) ₃ ·5 H ₂ O			Dy(Hsal) ₃ ·2 H ₂ O		
<i>T</i> range (K)	<i>T</i> _p (K)	ΔH (kJ mol ⁻¹)	<i>T</i> range (K)	<i>T</i> _p (K)	ΔH (kJ mol ⁻¹)
<i>Stage I</i>					
298–405	372	314.3	300–415	403	164.8
<i>Stage II</i>					
480–540	523	141.4	473–538	526	123.6
<i>Stage III</i>					
538–852	692	-4825	538–856	620	-4308

metal salicylates. The second significant difference between the studied dysprosium complexes and the transition metal complexes is that the thermal stability region of the anhydrous phase is slightly longer for the dysprosium compounds. The peak splitting at the third stage and the intensity of the endothermic (stage II) and exothermic (stage III) decomposition processes also deviate from the thermal behaviour of the transition metal salicylates.

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