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

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ABSTRACT

The thermal stability and mechanism of thermal decomposition in air of the four lanthanide complexes of 2-hydroxybenzoic acid have been studied by TG, DSC, IR and MS techniques. An analysis of the prepared compounds show that Pr(III), Nd(III) and Tb(III) form anhydrous salicylato (Hsal)⁻ complexes while the corresponding holmium compound contains four water molecules. The TG curves show two (praseodymium, terbium), three (neodymium) or four (holmium) main stages of thermal decomposition. The most unstable among the complexes studied is $Ho(Hsal)_3 \cdot 4H_2O$ which releases four water molecules in an endothermic dehydration step. Ligand molecules decompose mainly in two stages of which the first is endothermic and is attributed to the release of the ligand acid and the second is a strongly exothermic decarboxylation process. The final decomposition product is the corresponding lanthanide(III) oxide, except in the case of terbium which decomposes to Tb_4O_7.

INTRODUCTION

The study of complexation of lanthanide elements by salicylato ions is important because the bonding in such complexes can serve as a simple model for the interaction of these elements with humic materials in the natural environment. These materials are products of plant decomposition and are characterized chemically as complex polymers containing benzene rings with varying numbers of carboxyl and hydroxyl groups attached in a wide variety of combinations. The salicylato ion $C_7H_5O_3^-$ (Hsal)⁻ contains both the carboxylic and hydroxy functional groups and complexes with this ion represent bonding typical of the more complicated, natural materials [1].

A characteristic of the coordination chemistry of lanthanides is their pronounced tendency to form stable complex compounds with ligands containing oxygen as a donor atom. A comparison of the tendency of donor atoms to form complexes with most transition metals and with the lanthanides shows that with the transition metals the sequence is $N > S > O$, whereas with the lanthanides the sequence is $O > N > S$. After testing these

complexing properties with several organic ligands, the best results were obtained with hydroxycarboxylic acids [2].

Only a few crystal structures of salicylato complexes of trivalent lanthanides and actinides have been determined. Burns and Baldwin [3] have prepared and determined the crystal structure of $(C_7H_5O_3)_3Sm \cdot H_2O$ and $(C_7H_5O_3)_3Am \cdot H_2O$. According to their studies, the two complexes are isostructural and monoclinic having a space group P2$_1$/c. We have earlier studied the thermal behaviour and decomposition mechanism of some transition metal salicylato complexes and observed that also the Mn^{2+}, Ni^{2+} and Cu^{2+} ions with salicylate ion in acidic solution produce complexes which are monoclinic and belong to the space group P2$_1$/c but they are not isomorphous [4]. Recently, we have reported the thermal behaviour of salicylato, 5-chlorosalicylato and 5-bromosalicylato complexes of trivalent dysprosium and erbium ions [5–6].

EXPERIMENTAL

Reagents

The Ln_2O_3 (Ln = Nd, Tb, Ho) and Pr_6O_{11} of 99.9% purity were obtained from Fluka AG. The salicylic acid (H_2sal), extra pure grade, was supplied by Merck.

Preparation of compounds

For the syntheses the lanthanide oxides were transformed into sulphates [7]. Tris(salicylato) praseodymium(III) (A), tris(salicylato) neodymium(III) (B), tris(salicylato) terbium(III) (C) and tris(salicylato) holmium(III) tetrahydrate (D) were made by reaction of $Ln_2(SO_4)_3 \cdot 8H_2O$ (Ln = Pr, Nd, Tb, Ho) and $Na(C_7H_5O_3)$ in aqueous solution. The pH of the solutions after mixing was adjusted to 5.5, 5.3, 5.1 and 5.1 for the preparation of the compounds (A)–(D) respectively. Pale green (A), pale violet (B), white (C)

TABLE 1

Analytical data

Compound		Ln (wt.%)		H (wt.%)		C (wt.%)	
		Calc.	Found	Calc.	Found	Calc.	Found
Pr(Hsal)$_3$	(A)	25.5	25.6	2.7	3.1		
Nd(Hsal)$_3$	(B)	26.0	28.8	2.7	3.0		
Tb(Hsal)$_3$	(C)	27.9	27.0	2.7	2.8		
Ho(Hsal)$_3 \cdot 4H_2O$	(D)	25.4	25.3	3.6	4.3	38.9	36.0

and white (D) needles were formed. The products were washed, dried and analysed as described previously [6]. The analytical data of the complexes (A)–(D) are given in Table 1.

Instrumental

TG runs were carried out on a Mettler TG 50 thermobalance in air at a flow rate of 200 cm^3 min^{-1} using a heating rate of 5 K min^{-1}. ΔH measurements were performed on a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5 K min^{-1} under an air atmosphere (50 cm^3 min^{-1}). IR spectra were measured in a KBr matrix on a Perkin–Elmer 457 grating spectrometer in the range 250–4000 cm^{-1}. The mass spectra of the complexes and the decomposition products were recorded at a scanning rate of 1 s per decade on a Kratos MS 80 RF mass spectrometer, using the direct inlet system where the sample was heated at a rate of 50 K min^{-1}.

RESULTS AND DISCUSSION

The elemental chemical analyses agree with the formulae assumed for the complexes (A)–(D). The IR spectra of Pr(III), Nd(III) and Tb(III) salicylato complexes are very similar and in practice they coincide. Although the IR spectra of Pr(Hsal)$_3$ and Ho(Hsal)$_3 \cdot 4H_2O$ seem to be quite similar (Fig. 1), they show at least one clear difference. For Ho(Hsal)$_3 \cdot 4H_2O$, there is a band at 3600 cm^{-1} which is characteristic of free OH. However, for Dy(III), Er(III) and Ho(III) salicylato complexes, all containing water molecules, the
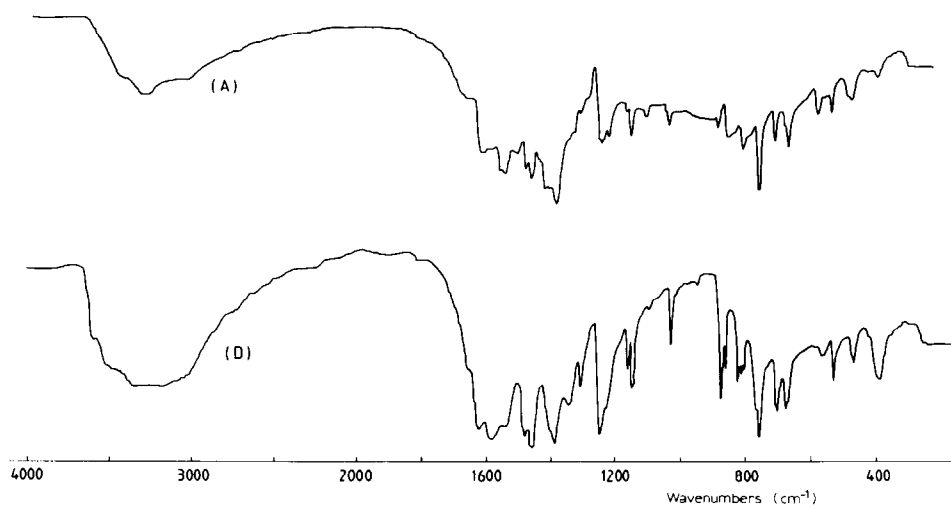

Fig. 1. IR spectra of Pr(Hsal)$_3$ (A) and Ho(Hsal)$_3 \cdot 4H_2O$ (D).
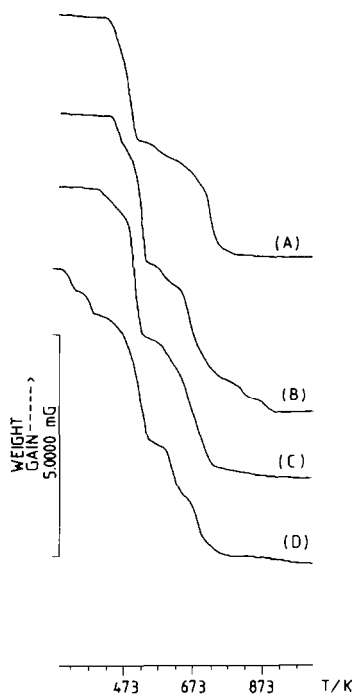
Fig. 2. TG curves of Pr(Hsal)$_3$ (A), Nd(Hsal)$_3$ (B), Tb(Hsal)$_3$ (C) and Ho(Hsal)$_3\cdot$4H$_2$O (D).

IR spectra show a band of a frequency corresponding to free OH [5,6]. It is worth noticing that this band is absent not only for the anhydrous Pr(III), Nd(III) and Tb(III) salicylato complexes (Fig. 1), but also for the hydrated 5-substituted Dy(III) and Er(III) salicylato complexes as well as hydrated Co(II), Cu(II), Mn(II), Zn(II) and Ni(II) salicylato complexes [4,6]. This means that the OH stretching vibration band at 3600 cm^{-1} cannot be attributed entirely or exclusively to the water, but must also arise from the phenolic hydroxide groups. On the basis of IR spectra we can suppose that the crystal structure of Ho(III), Er(III) and Dy(III) salicylato complexes are

TABLE 2

TG data on the decomposition of lanthanide salicylato complexes

Compound		Stage I			Stage II		
		T range (K)	T_p (K)	Loss in weight (%)	T range (K)	T_p (K)	Loss in weight (%)
Pr(Hsal)$_3$	(A)	–	–	–	419–536	499	35.9
Nd(Hsal)$_3$	(B)	–	–	–	428–554	526	35.7
Tb(Hsal)$_3$	(C)	–	–	–	394–549	504	35.6
Ho(Hsal)$_3\cdot$4H$_2$O	(D)	295–392	380 [a]	11.0	392–571	528	31.3

[a] The main peak of double recorded by TG. T_p is the peak maximum/minimum temperature.
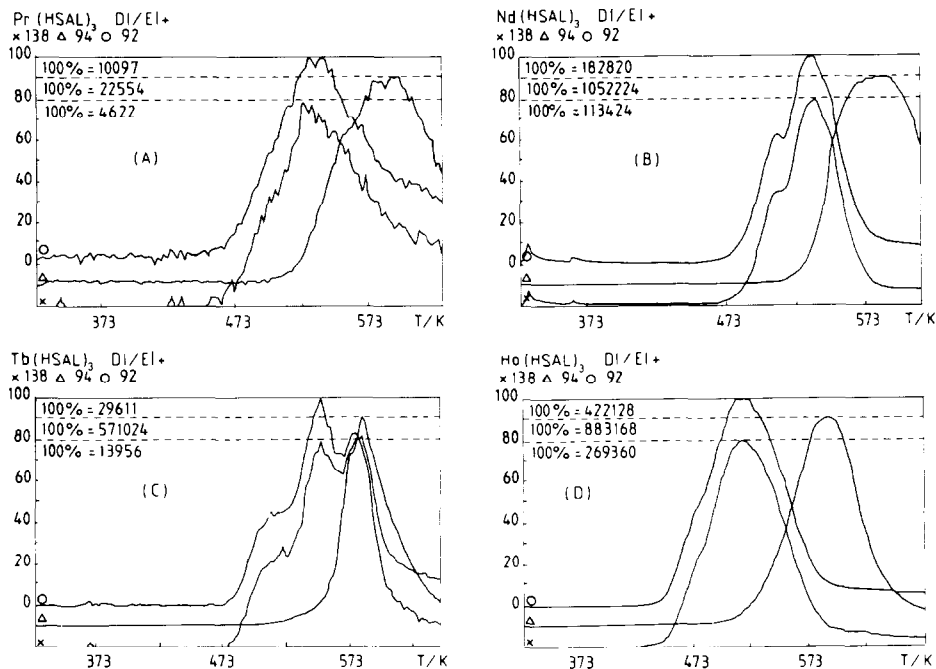
Fig. 3. Mass chromatograms of the complexes (A)–(D). The ions 138 and 92 (M/z) are attributed to a salicylic acid and the ion 94 (M/z) to a phenol. DI/EI+ means direct inlet/electron ionization.

very similar. One explanation of the presence of the IR band at 3600 cm^{-1} may be that the crystal structure of Ho(III), Er(III) and Dy(III) salicylato complexes are unchelated. The detailed IR analysis of the other bands have been presented earlier in the case of other lanthanide salicylato complexes [5,6].

In air the thermal decomposition of the complexes (A) and (C) occurs in two stages and that of the complexes (B) and (D) in three and four stages respectively (Fig. 2). The dehydration process of the complex (D) takes place

Stage III			Stage IV			Residue (wt.%)	
T range (K)	T_p (K)	Loss in weight (%)	T range (K)	T_p (K)	Loss in weight (%)	Calc.	Found
536–803	722	32.7	–	–	–	29.9	29.7
554–854	657	31.9	854– 909	890	2.8	30.3	29.6
549–814	659	31.3	–	–	–	32.8	33.1
571–773	684 [a]	26.6	823–1013	923	1.7	29.1	29.4

TABLE 3

Enthalpy changes ΔH for the thermal decomposition of lanthanide salicylato complexes

Compound		Stage I			Stage II			Stage III		
		T range (K)	T_p (K)	ΔH (kJ mol^{-1})	T range (K)	T_p (K)	ΔH (kJ mol^{-1})	T range (K)	T_p (K)	ΔH (kJ mol^{-1})
Pr(Hsal)$_3$	(A)	–	–	–	443–533	470 [a]	159.7	553–790	767 [a]	– 4484
Nd(Hsal)$_3$	(B)	–	–	–	443–534	524 [a]	173.8	534–773	745 [a]	– 3798
Tb(Hsal)$_3$	(C)	–	–	–	417–539	521 [a]	170.0	539–777	727 [a]	– 4184
Ho(Hsal)$_3 \cdot 4H_2O$	(D)	298–410	396	258.3	473–544	531	167.9	544–772	624 [a]	– 3759

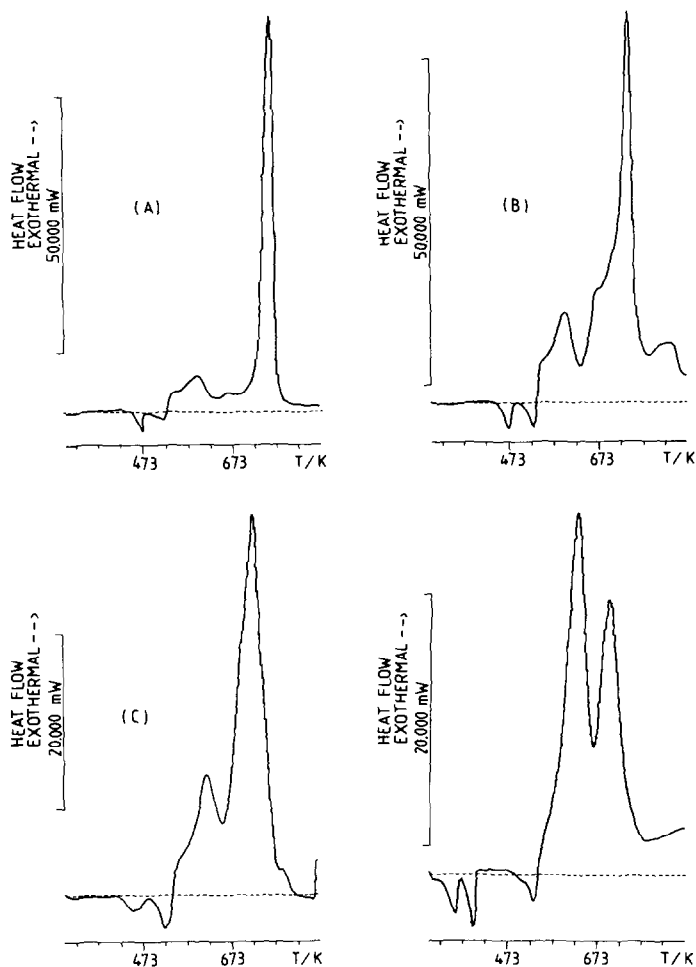[a] The main peak of doublet. T_p is the peak maximum/minimum temperature.

Fig. 4. DSC curves of the complexes (A)–(D).

in two successive stages which correspond exactly to the loss of four water molecules (Table 2). Since the first two water molecules are released below 350 K we can deduce that some of the water molecules are not coordinately bound. It is interesting to observe that the energy required to release these four water molecules (Table 3) is as great as in the case of $Er(Hsal)_3 \cdot 4H_2O$.

The anhydrous complexes (A)–(D) decompose between 417 and 544 K, the peak maximum being at the same temperature as that mentioned earlier in connection with Dy(III) and Er(III) salicylato complexes [5,6]. The mass spectra and mass chromatograms (Fig. 3) recorded using a direct inlet system show that the main decomposition product in this stage is the salicylic acid ($M/z = 138$). The weight loss in this decomposition step corresponds to the release of one and a half ligand acid molecule for all complexes (A)–(D). Figure 4 reveals that there is a doublet peak in the DSC curves of complexes (A)–(C) which shows the existence of two successive

stages in the release of ligand acid from the crystal structure of the mentioned complexes. The ΔH values of the release of salicylic acid from the crystal structure of the complexes (A)–(D) agree well with the values measured for $Dy(Hsal)_3 \cdot 2H_2O$ and $Er(Hsal)_3 \cdot 4H_2O$ [5,6].

In the third decomposition stage (the second for complexes (A)–(C)) between 536 and 854 K a decarboxylation occurs which according to our TG results corresponds in all cases to the release of 1.3 molecules of salicylic acid. Figure 4 shows that again the complex (D) deviates from the behaviour of the others. For complexes (A)–(C) the main peak of this decomposition step is below 673 K while for the $Ho(Hsal)_3 \cdot 4H_2O$ the situation is the opposite. However, we again draw attention to the closely similar thermal behaviour of $Dy(Hsal)_3 \cdot 2H_2O$, $Er(Hsal)_3 \cdot 4H_2O$ and $Ho(Hsal)_3 \cdot 4H_2O$. It is interesting to observe that the ΔH values of Pr(III), Nd(III), Tb(III), Dy(III), Ho(III) and Er(III) salicylato complexes are quite close to each other and the most exothermic ΔH values of the third stage can be attributed to the Pr(III) complex, and correspondingly, the least exothermic to the Ho(III) complex.

In the last stage before the formation of Nd_2O_3 and Ho_2O_3, the combustion of the remaining organic material occurs corresponding to the release of 0.1 molecules of salicylic acid. For complexes (A) and (B) the final decomposition products are Pr_2O_3 and Nd_4O_7. The values of residue (wt.%) (Table 2) agree very well with the mentioned oxides.

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