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SOLID STATE DECOMPOSITION STUDIES ON METAL SALICYLATES. THERMAL DECOMPOSITION OF THE 5-SUBSTITUTED DYSPROSIUM AND ERBIUM SALICYLATO COMPLEXES

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ABSTRACT

The thermal decomposition of the dysprosium and erbium salicylates, and 5-chloro and 5-bromosalicylates was studied by TG, DSC, IR and MS techniques. The various dysprosium salicylates were precipitated from aqueous solution as dihydrates and the corresponding erbium salicylates as tetrahydrates. The TG curves show four steps of decomposition. The decomposition reaction mechanism of the complexes was studied by analyzing the intermediate products with mass and IR spectrometry. The first three stages for all the complexes are associated with the dehyration, the release of free ligand acid and the release of ligand acid by decarboxylation. The 5-chlorosubstituted salicylato complexes were thermally more stable than unsubstituted or 5-bromosubstituted salicylato complexes. For each complex, the first two steps are endothermic, while the third step is strongly exothermic. The oxides, Ln_2O_3, were obtained in the temperature range 938–1023 K. The temperature for oxide formation seems to follow the order salicylic acid > 5-chlorosalicylic acid > 5-bromosalicylic acid.

INTRODUCTION

Considerable attention has been paid recently to the synthesis and structure of organolanthanides because of their many applications, such as hydrogen storage, solid state lasers, and analytical methods. The most studied organolanthanides are those of neodymium, cerium, lanthanum and ytterbium in that order. This order represents both the availability of the *f*-block elements and their ability to form crystals [1]. The most common coordination numbers of the lanthanides are 8 and 9.

We have studied thermal behaviour of transition metal salicylates in a series of investigations in order to understand the mechanisms of decomposition and the nature of the decomposition products [2–6]. Recently we initiated a new series of investigations concerning the complex formation and thermal behaviour of the lanthanide salicylates by publishing the results attributed to dysprosium salicylato complexes [7]. As a continuation of our

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work, we now report data obtained from the thermal decompositions of dysprosium and erbium salicylates, 5-chlorosalicylates and 5-bromosalicylates.

EXPERIMENTAL

Reagents

The dysprosium and erbium oxides (at least 99.9% pure) were obtained from Fluka AG. The salicylic acid (H_2sal) was extra pure grade (Merck), 5-chlorosalicylic (5-ClH_2sal) and 5-bromosalicylic (5-BrH_2sal) acids were purum grade (Fluka AG).

Preparation of the lanthanide compounds

Dysprosium and erbium sulfates, $Ln_2(SO_4)_3 \cdot 8H_2O$, were used as starting materials, and were prepared as described previously by Wendlandt [8]. The Dy(5-ClHsal)$_3 \cdot 2H_2O$ and Dy(5-BrHsal)$_3 \cdot 2H_2O$ complexes were prepared as described earlier except that the final pH of the solution containing $Dy_2(SO_4)_3$ and sodium salicylate was adjusted to 4.66 and 4.38, respectively [7]. The grey crystals were precipitated at room temperature over 1 h. The Er(Hsal)$_3 \cdot 4H_2O$, Er(5-ClHsal)$_3 \cdot 4H_2O$ and Er(5-BrHsal)$_3 \cdot 4H_2O$ complexes were prepared by adding 0.022 M $Er_2(SO_4)_3$ solution (pH 4.8–5.6) to a 0.3 M sodium salicylate (5-chloro-, 5-bromosalicylate, respectively) solution (pH 6.0–6.6) in the molar ratio 1 : 3. The pH of the resulting erbium salicylate and erbium-5-chloro- and -5-bromosalicylate solutions were adjusted to 5.1, 4.4 and 4.2, respectively with NaOH and H_2SO_4 solutions. The precipitation of pink Er(Hsal)$_3 \cdot 4H_2O$, Er(5-ClHsal)$_3 \cdot 4H_2O$ and Er(5-BrHsal)$_3 \cdot 4H_2O$ crystals took about two days at room temperature and under the cover of a thin parafilm. After filtration the crystals of the dysprosium and erbium compounds were washed twice with 20 ml of water

TABLE 1

Analytical data

Compound	M (%)		H (%)		C (%)	
	Found	Calc.	Found	Calc.	Found	Calc.
Dy(5-ClHsal)$_3 \cdot 2H_2O$ (A)	22.8	23.9	2.3	2.1		
Dy(5-BrHsal)$_3 \cdot 2H_2O$ (B)	19.2	19.0	1.9	2.0		
Er(Hsal)$_3 \cdot 4H_2O$ (C)	24.2	25.7	3.9	3.6		
Er(5-ClHsal)$_3 \cdot 4H_2O$ (D)	22.3	22.2	2.2	2.7	33.0	33.4
Er(5-BrHsal)$_3 \cdot 4H_2O$ (E)	19.0	18.9	2.1	2.3	27.4	28.4

and once with 20 ml of 95% ethanol. Thereafter the products were filtered off and dried in a vacuum desiccator at room temperature. Analytical data of the complexes are given in Table 1.

Instrumentation

TG and DSC runs were carried out on a Mettler TA 3000 thermal analysis system as described earlier [7]. The metal content of the compounds were determined by DCP-AES (Spectra Span IIIB), hydrogen content with an element analyzer (Leco RH2) and carbon content by the method described earlier [9]. IR spectra were measured in a KBr matrix on a Perkin-Elmer 457 grating spectrometer. 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 sample at a rate of 50 K min^{-1}.

RESULTS AND DISCUSSION

The IR spectra of the corresponding dysprosium and erbium salicylato complexes are similar to each other (Figs. 1 and 2) [7]. However, clear differences between unsubstituted and substituted salicylato complexes can

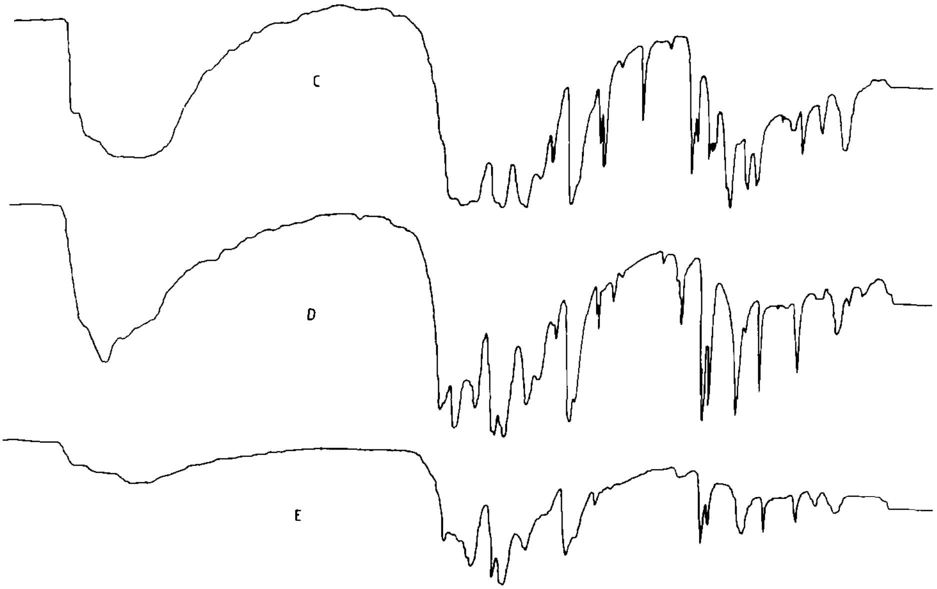

Fig. 1. IR spectra of (C) $Er(Hsal)_3 \cdot 4H_2O$, (D) $Er(5\text{-}ClHsal)_3 \cdot 4H_2O$ and (E) $Er(5\text{-}BrHsal)_3 \cdot 4H_2O$.

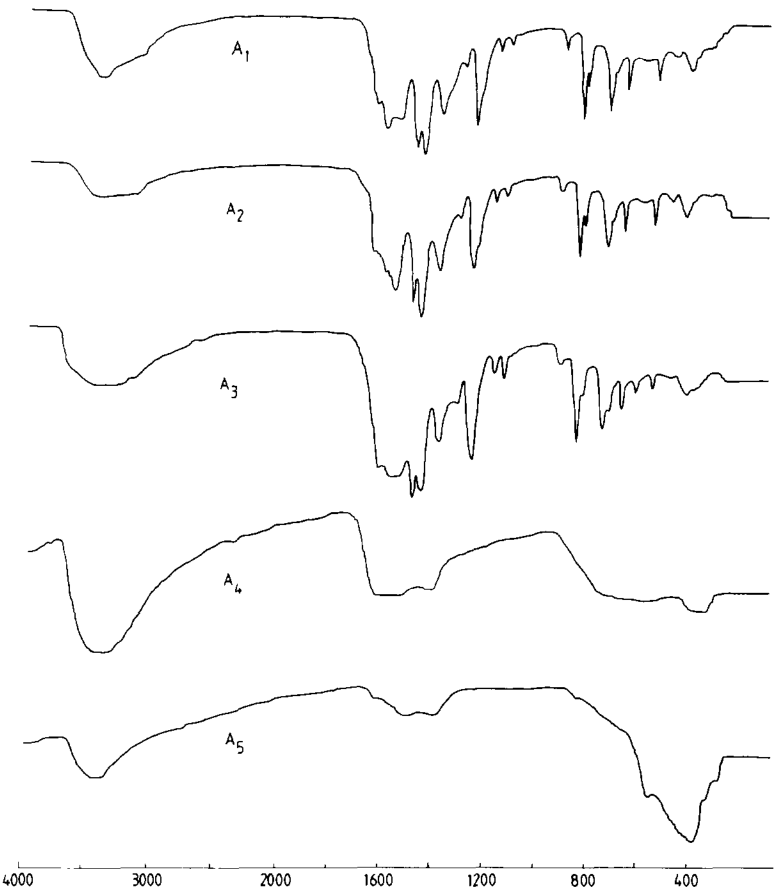

Fig. 2. IR spectra of $Dy(5\text{-}ClHsal)_3 \cdot 4H_2O$. The letters A_1, A_2, A_3, A_4 and A_5 refer to the temperatures of 293, 423, 568, 773 and 1023 K, respectively.

be seen. The IR spectra of solid substituted and unsubstituted lanthanide salicylato complexes can be divided into following regions: 3600–2800 cm^{-1}, the stretching absorptions of the free OH-groups originating both from water molecules and from phenol groups; 1650–1435 cm^{-1} (1640–1400 cm^{-1}, containing both the C–O stretching of the carboxyl group and C=C stretching vibrations of the benzene ring; 1430–1350 cm^{-1} (1390–1310 cm^{-1}), the C–O–H bending of the phenol group; 1260–1170 cm^{-1} (1255–1165 cm^{-1}) stretching of the phenol group; 540–515 cm^{-1}, out of plane bending vibrations of the benzene ring and the bands of the metal–oxygen bond at 430–380 cm^{-1}. The values in parentheses represent the bands of 5-chloro and 5-bromolanthanide complexes. At 930–610 cm^{-1} the IR spectra of $Ln(5 - x\text{Hsal})_3 \cdot nH_2O$ (x = H, Cl, Br, Ln = Er, Dy, $n = 2$ or 4) complexes are dependent on the substituent while the effect of the same substituent is similar for both dysprosium and erbium complexes. In

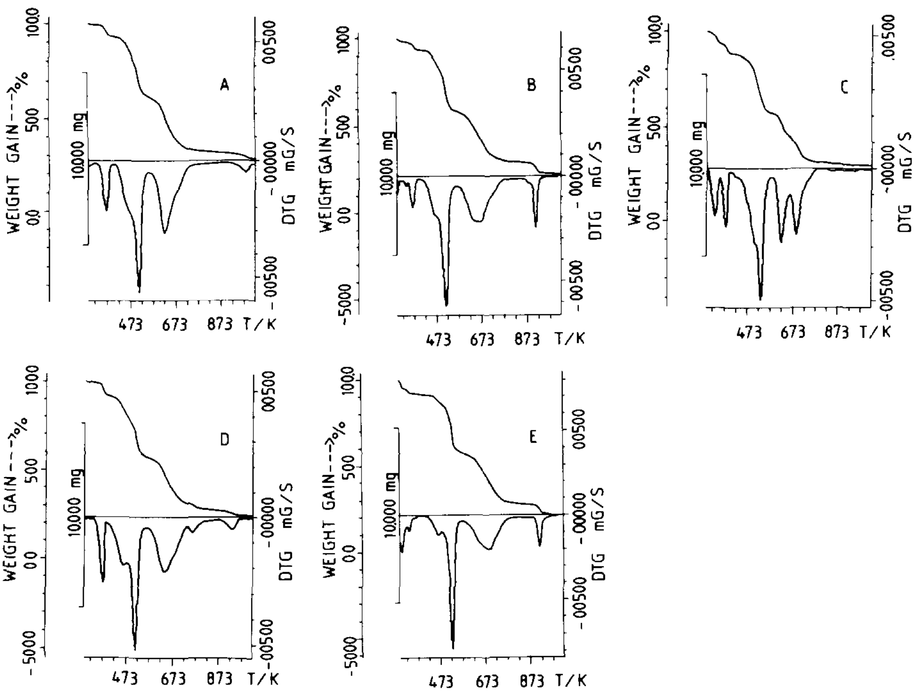

Fig. 3. TG curves of (A) $Dy(5\text{-}ClHsal)_3 \cdot 2H_2O$, (B) $Dy(5\text{-}BrHsal)_3 \cdot 2H_2O$, (C) $Er(Hsal)_3 \cdot 4H_2O$, (D) $Er(5\text{-}ClHsal)_3 \cdot 4H_2O$ and (E) $Er(5\text{-}BrHsal)_3 \cdot 4H_2O$.

the case of erbium and dysprosium salicylates the bands at 880, 820, 755, 700 and 675 cm^{-1} are due to out-of-plane bending vibrations of the benzene ring, while for the dysprosium and erbium 5-chlorosalicylato complexes the bands at 890, 830 and 650 cm^{-1} are attributed to out-of-plane bending vibrations of the benzene ring but the band at 720 cm^{-1} originates from the C–Cl bending vibration. For the 5-bromosalicylato complexes the bands at 830 and 630 cm^{-1} are due to out-of-plane bending vibrations of the benzene ring and the band at 695 cm^{-1} from the C–Br bending vibration respectively. Analysis of the IR spectra supports the chemical analyses of the compositions of the complexes. In air the thermal decomposition of the complexes (A)–(E) occurs in four stages (Fig. 3). The part and significance of the fourth stage is minor in the case of dysprosium [7] and erbium complexes but increases with increasing atomic number of the substituent (Table 2). The first two steps are endothermic and the third step is strongly exoethermic (Fig. 4). The first stage of thermal decomposition of the complexes (A)–(E) is the dehydration process. The weight losses of the dehydration process agree with the compositions of the complexes (A)–(E).

Thermally the most stable of the complexes (A)–(E) are $Dy(5\text{-}ClHsal)_3 \cdot 2H_2O$ and $Er(5\text{-}ClHsal)_3 \cdot 4\ H_2O$ while in the corresponding 5-bromo substituted complexes the loss of water molecules occur at quite low tempera-

TABLE 2

TG data from the decomposition of dysprosium and erbium salicylato complexes

Compound	Stage I			Stage II			Stage III			Stage IV			Residual weight (%)	
	T range (K)	T_p (K)	Weight loss (%)	T range (K)	T_p (K)	Weight loss (%)	T range (K)	T_p (K)	Weight loss (%)	T range (K)	T_p (K) (K)	Weight loss (%)	Calc.	Found.
Dy(5-ClHsal)$_3$ $\cdot 2H_2O$ (A)	334–397	372	6.3	397–551	551	30.9	551–787	622	29.9	920–1020	983	3.1	26.2	27.0
Dy(5-BrHsal)$_2$ $\cdot 2H_2O$ (B)	341–385	366	3.9	386–559	514	34.6	559–768	666	29.4	768– 938	910	7.7	22.0	22.4
Er(Hsal)$_3$ $\cdot 4H_2O$ (C)	296–389	378 [a]	11.2	398–570	529	30.8	573–765	620 [a]	26.8	733–1023	938	1.9	29.4	29.3
Er(5-ClHsal)$_3$ $\cdot 4H_2O$ (D)	338–388	376	7.4	388–559	516	34.1	559–850	638	30.2	880– 956	933	2.5	25.3	25.8
Er(5-BrHsal)$_3$ $\cdot 4H_2O$ (E)	294–372	304	8.1	418–574	530	33.8	574–849	693	30.3	849– 949	915	6.2	21.6	21.6

[a] Main peak of two successive peaks in Fig. 1.

TABLE 3

Enthalpy changes, ΔH, for the decomposition of the 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})
Dy(5-ClHsal)$_3$$\cdot 2H_2O$ (A)	370–426	408	123.9	445–539	531	80.5	539–780	659	−3371
Dy(5-BrHsal)$_3$$\cdot 2H_2O$ (B)	303–414	399 [a]	140.3 [b]	458–545	535	99.3	545–816	687	−3721
Er(Hsal)$_3$$\cdot 4H_2O$ (C)	303–403	391 [a]	254.4 [b]	458–546	530	152.6	546–851	630 [a]	−4115
Er(5-ClHsal)$_3$$\cdot 4H_2O$ (D)	345–420	406	187.9	498–549	540	125.2	549–840	671	−3805
Er(5-BrHsal)$_3$$\cdot 4H_2O$ (E)	298–407	355	298.1	499–551	541	138.8	551–813	712	−3895

[a] Main peak of two successive peaks in Fig. 2.

[b] Total ΔH of two successive peaks.

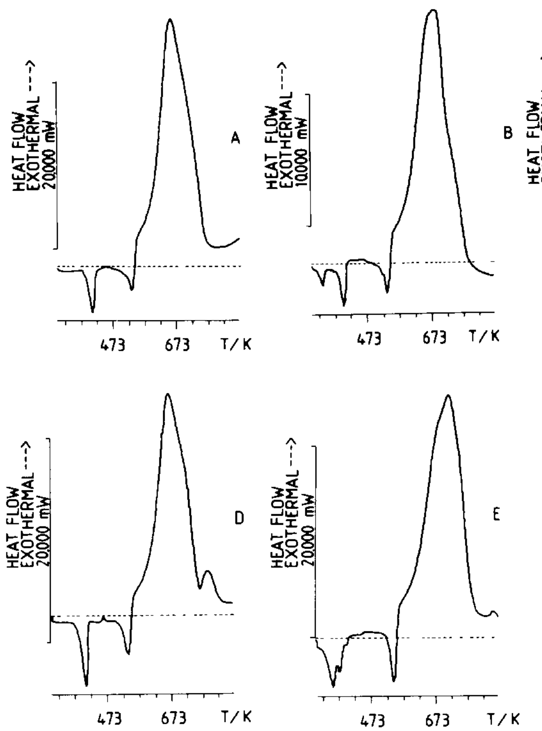

Fig. 4. DSC curves of complexes (A)–(E).

tures. A second interesting feature which is connected to the removal of four water molecules of the erbium compounds (C)–(E) is that the dehydration peak has clearly split into two parts in the case of complexes (C) and (E) (Figs. 3 and 4). The ΔH values of complexes (C) and (E) (Table 3) are greater ($\Delta H = 254$ and 298 kJ mol^{-1}) than for the complex (D) ($\Delta H = 188$ kJ mol^{-1}). Probably this means that the bonding of the water molecules in the structure of the complexes (C) and (E) is similar but clearly deviates in the case of complex (D). In addition, because the dehydration enthalpy of lanthanide salicylato complexes is about twice that of transition metal salicylato complexes, the interactions between the water molecules and Ln^{3+}-ions are stronger than the interactions between Me^{2+}-ions and H_2O molecules [5,7].

The anhydrous complexes (A)–(E) decompose between 400 and 570 K, the peak maximum being at about 525 K, exactly the same as for the dysprosium salicylato complex [7]. The mass spectra and mass chromatograms recorded by direct inlet system for the complex and the solid intermediate products shows that the main decomposition product in the second stage is the ligand acid, combined with the minor decarboxylation process (Fig. 5). The weight loss of the second stage corresponds to the loss

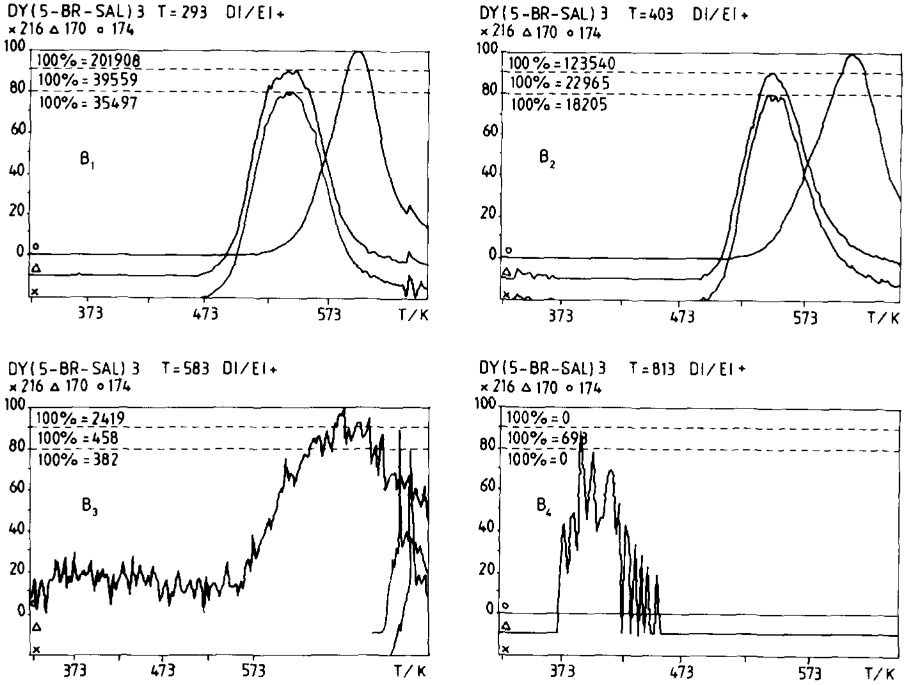

Fig. 5. Mass chromatograms of $Dy(5\text{-}BrHsal)_3\cdot 2H_2O$ taken from a pure complex and from the intermediate products. The letters B_1, B_2, B_3 and B_4 refer to temperatures of 293, 403, 583 and 813 K, respectively. The ions 216 and 170 (m/z) are attributed to the ligand acid and the ion 174 respectively to the bromophenol.

of 1.5 ligand acid molecules for unsubstituted and 5-chlorosubstituted dysprosium and erbium salicylato complexes, and the loss of 1.4 ligand acid molecules for the corresponding 5-bromosubstituted complexes (Table 2). The IR spectra of complex (A) shows that the frequencies attributed to C=O– and C=O– vibrations are seen also in the intermediate product at 568 K; in every way the IR spectra of this intermediate product resembles the IR spectra of anhydrous $Dy(5\text{-}ClHsal)_3$ (Fig. 2).

It should be noticed that the peak corresponding to the third decomposition stage has split for complex (C) only as in the case of $Dy(Hsal)_3\cdot 2H_2O$ [7], while for the complexes (A), (B), (D) and (E) the decarboxylation process seems to occur at one stage and to be the main decomposition mechanism of this decomposition stage (Fig. 5). The IR spectra of complex (A) at 773 K (Fig. 2) shows that the intermediate product of that stage contains only very little organic material which burns with oxygen to give Dy_2O_3. In the third step according to TG data n molecules of the ligand acid take part in the decarboxylation of salicylato ($n = 1$, 3), 5-chlorosalicylato ($n = 1$, 3) and 5-bromosalicylato ($n = 1$, 2) complexes of dysprosium and erbium metals. In the last stage before the formation of Dy_2O_3 or Er_2O_3 the combustion of the remaining organic material occurs corresponding to

0.1 moles of the ligand acid for the complexes (A), (C) and (D) and 0.3 moles of the ligand acid for the complexes (B) and (D).

The ΔH values of the stages II and III are respectively more endothermic and exothermic than the corresponding values of *d*-block metal salicylato or 5-substituted salicylato complexes [5,6]. On the basis of X-ray structural analysis of the complexes we will probably be able to interpret these differences in more detail.

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