

## THERMAL DECOMPOSITION OF COMPLEXES

$[\text{Co}(\text{NH}_3)_6](\text{M}^1)_3[\text{Ln}(\text{SO}_4)_3]_2 \cdot n\text{H}_2\text{O}$  ( $\text{M}^1 = \text{NH}_4, \text{Rb}; \text{Ln} = \text{La, Ce, Pr}$ )

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(Received 8 July 1987)

### ABSTRACT

Thermal decomposition of the trivalent lanthanide sulfato complexes of the composition  $[\text{Co}(\text{NH}_3)_6](\text{M}^1)_3[\text{Ln}(\text{SO}_4)_3]_2 \cdot n\text{H}_2\text{O}$ , where  $\text{M}^1 = \text{NH}_4$  ( $n = 3$ ) or  $\text{Rb}$  ( $n = 2$ ) and  $\text{Ln} = \text{La, Ce or Pr}$ , has been studied using a DTA–TG apparatus. When the complexes were heated from room temperature to  $600^\circ\text{C}$ , dehydration occurred at about  $215^\circ\text{C}$  followed at about  $320^\circ\text{C}$ , by decomposition in which the constituent  $[\text{Co}(\text{NH}_3)_6]$  took part. Unusually, in an atmosphere of air, the latter step was exothermic and the liberated  $\text{NH}_3$  was less than 1% of the total ammonia, whereas in an atmosphere of Ar it was endothermic, with evolution of 70% as  $\text{NH}_3$ .

### INTRODUCTION

In a previous paper [1] we reported that the hexaamminecobalt(III) complexes  $[\text{Co}(\text{NH}_3)_6][\text{Nd}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$  decompose exothermically in a dynamic air atmosphere at around  $300^\circ\text{C}$ . The liberation of heat was ascribed to oxidative deamination, since only a small fraction of the coordinated ammonia was found in the stream of air, whereas in an Ar atmosphere about 70% was liberated. Although there have been many investigations on the thermal decomposition of the metal ammine complexes, this type of exothermic change is rather rare. One example is given by  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ , which decomposes by exothermic reaction even in an inert atmosphere; it was reported that 25% of the total  $\text{NH}_3$  was liberated by its decomposition [2]. We reported that various types of sulfato complexes containing the hexaamminecobalt(III) cation are obtained for the lanthanides [3] and the actinides in different oxidation states [4]. For the trivalent lanthanides yttrium and scandium the complexes have a similar composition to that given for Nd(III) above. Preliminary thermal analysis study showed all the complexes decomposed by exothermic reaction in the air. From these experiments, the deamination reactions of hexaamminecobalt(III) complexes are expected to be influenced by the constituents in the outer-sphere of Co(III). Thus it will be of value to study complexes of different composi-

tions under similar conditions. For the light lanthanides, La, Ce and Pr, complexes of a more complicated structure as given by the general formula  $[\text{Co}(\text{NH}_3)_6](\text{M}^1)_3[\text{Ln}(\text{SO}_4)_3]_2 \cdot n\text{H}_2\text{O}$  ( $\text{M}^1 = \text{NH}_4$  or Rb) crystallize in aqueous solutions which contain the sulfate of each cation. Since monovalent cations  $\text{NH}_4^+$  and  $\text{Rb}^+$  are of equivalent size, the structures of these complexes seem to be very close. In spite of this, their thermal behavior and IR spectral properties must be somewhat different. The present study was carried out for this type of complex. By applying the techniques used for the Nd(III) complexes (DTA-TG measurements, determination of evolved ammonia, X-ray diffraction and IR spectral studies) the decomposition intermediates were investigated.

## EXPERIMENTAL

### *Preparation of the complexes*

Stock solutions of trivalent lanthanide chlorides were prepared by dissolving the respective oxides in a solution of hydrochloric acid. After removing the excess acid by evaporation, the residues were dissolved in water. The aqueous solutions of 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  were prepared to contain 0.02 M  $\text{LnCl}_3$ . To the solutions, 0.1 M  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  solution was added to give a  $[\text{Co}(\text{NH}_3)_6]^{3+}$  concentration of  $5 \times 10^{-3}$  M. After a week or two, yellow needle-like crystals were taken out and washed with water and dried in a desiccator under vacuum. To prepare the complexes which contain  $\text{Rb}^+$ , 0.38 M  $\text{Rb}_2\text{SO}_4$  solutions were used instead of the ammonium sulfate solution. The other part of the procedure was the same as above. Because the double sulfates of  $\text{Rb}^+$  and Pr(III) precipitated with the complex, pure materials were not obtained. Constituents of five complexes were analysed for Co, Ln,  $\text{NH}_4$ , Rb and  $\text{SO}_4$  using the standard methods. The results of the analyses and the calculated values for the proposed formula are given in Table 1. Hereafter the abbreviated notation as given in Table 1 will be used to indicate each complex.

### *Thermal analysis*

DTA and TG curves were recorded simultaneously with a "Thermoflex" instrument (Rigaku Denki Co.) from room temperature to  $600^\circ\text{C}$ . A detailed description of its structure and the procedure have been given in a previous paper [1]. All the complexes were crushed with an agate mortar to particle size suitable for packing in a platinum crucible 5 mm in diameter and 5 mm in height.

Determination of the ammonia evolved on heating of the complexes was by the same procedure used in the study of the Nd(III) complexes. IR

TABLE 1

Analytical results of the complexes <sup>a</sup>

Complex	Co (%)	NH <sub>4</sub> /Rb (%)	Ln (%)	SO <sub>4</sub> (%)	H <sub>2</sub> O (%)
La-NH <sub>4</sub>	5.38(5.25)	4.55(4.82)	25.14(24.73)	50.51(51.30)	5.09(4.81)
Ce-NH <sub>4</sub>	5.24(5.23)	4.51(4.81)	24.55(24.89)	50.68(51.19)	5.94(4.80)
Pr-NH <sub>4</sub>	5.29(5.23)	4.72(4.80)	25.44(25.00)	50.97(51.12)	4.40(4.79)
La-Rb	4.46(4.51)	19.90(19.61)	20.63(21.24)	44.73(44.07)	2.55(2.76)
Ce-Rb	4.09(4.50)	19.99(19.57)	21.18(21.39)	44.92(43.99)	2.73(2.75)

<sup>a</sup> Values in parentheses are calculated for the formula [Co(NH<sub>3</sub>)<sub>6</sub>](NH<sub>4</sub>)<sub>3</sub>[Ln(SO<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·3H<sub>2</sub>O and for [Co(NH<sub>3</sub>)<sub>6</sub>](Rb)<sub>3</sub>[Ln(SO<sub>4</sub>)<sub>3</sub>]<sub>2</sub>·2H<sub>2</sub>O.

spectra and X-ray powder diffraction patterns of the intermediates were measured by the standard techniques.

## RESULTS AND DISCUSSION

All the complexes were obtained as yellow needle-like crystals. Morphological observation of their external shapes predicted that they would be isostructural. The X-ray powder patterns proved that the complexes with NH<sub>4</sub><sup>+</sup> and those with Rb<sup>+</sup> are isostructural to each other, though indexing of each pattern has not yet been tried. Since main *d*-values commonly exist for the complexes with NH<sub>4</sub><sup>+</sup> and with Rb<sup>+</sup> their crystal structures will be very closely related. The IR spectra in the 2000–300 cm<sup>-1</sup> region of these complexes will show absorption bands due to H<sub>2</sub>O, NH<sub>4</sub>, SO<sub>4</sub> and NH<sub>3</sub>. Of these bands the splitting of the IR active  $\nu_3$  and  $\nu_4$  bands of the sulfate ion will provide information about its coordination properties. Actually, clear splitting of  $\nu_4$  into two will indicate that the sulfate ions are primarily of monodentate character. Moreover there are two well-separated absorption bands at 1345 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>, both of which will be ascribed to the nondegenerate symmetric deformation of the coordinated ammonia [5]. This might suggest that the octahedral [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> ions exist in an environment of marked anisotropic nature.

The DTA and TG curves for all five complexes were measured both under the air flow and under the Ar gas flow at the same rate of 100 ml min<sup>-1</sup>. All the complexes showed essentially the same pattern, as typically given in Figs. 1 and 2 for the La(III) complexes. In the DTA curves obtained under flowing air we can observe two exotherms at about 300 and 340 °C following an endotherm at 210 °C. At higher temperature Ln-NH<sub>4</sub> further decomposed in the air flow with a relatively small heat change of ambiguous nature, whereas Ln-Rb remained as intermediates which were stable up to at least 600 °C. Under the Ar gas flow, the decomposition of each complex produced only endotherms throughout the temperature range studied.

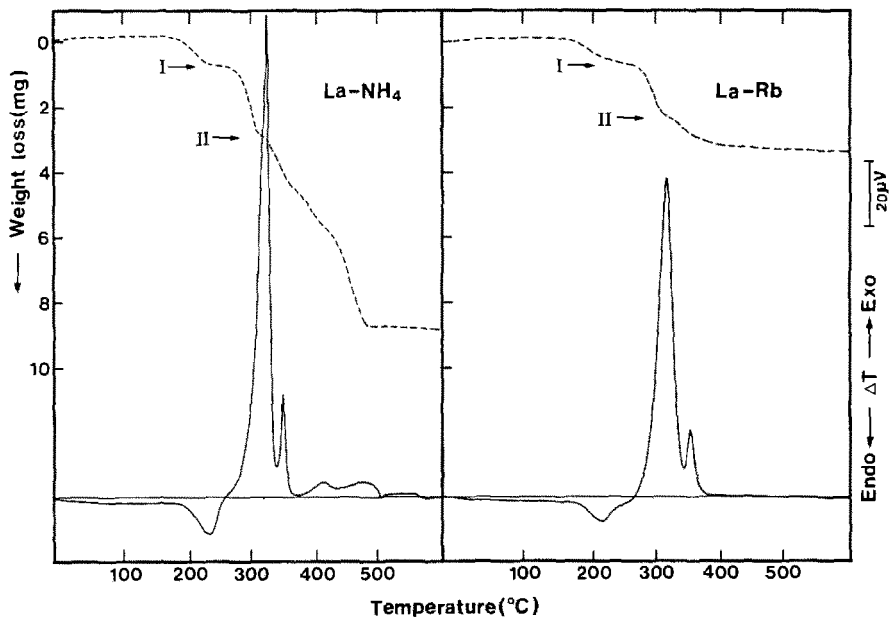


Fig. 1. DTA (solid line) and TG (broken line) curves of the La(III) complexes under air flow. Sample amount: La-NH<sub>4</sub>, 26.06 mg; La-Rb, 24.75 mg.

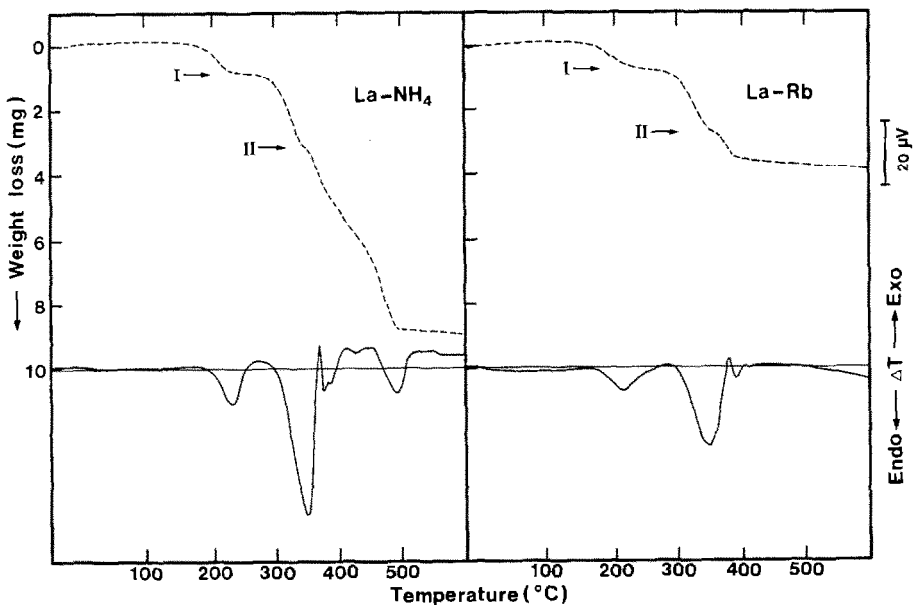


Fig. 2. DTA (solid line) and TG (broken line) curves of the La(III) complexes under Ar gas flow. Sample amount: La-NH<sub>4</sub>, 25.45 mg; La-Rb, 25.83 mg.

In accord with the DTA curves, there are a few plateaus in the TG curves. The first one, indicated as I in the figures, appears after the endothermic decomposition and the second one, indicated as II in the figures, appears after the exothermic reaction (or endothermic reaction in the Ar gas flow). For Ln-NH<sub>4</sub> there are inflections, though these are not obvious, in the TG curves at higher temperature. Therefore, further decomposition of the intermediate formed at II may be expected to be fairly complicated. In contrast, Ln-Rb seems to decompose in just three steps in this temperature range.

As our main interest concerns the decomposition involving hexaamminecobalt(III) cation, further discussion will be concentrated on the first and the second stages of the decomposition. Thus the temperature at the peak ( $T$ ) and the weight loss ( $\Delta W$ ) due to the first and second stage decompositions were read at the plateaus I and II in the figures as presented in Table 2. Table 2 shows that for each series of complexes the peak temperatures of the first stage decomposition are very close to each other and are unaffected by the atmosphere. When compared with those for Ln-Rb, the temperatures for Ln-NH<sub>4</sub> are nearly 20°C higher in both atmospheres. On the other hand, the influence of the atmosphere is obvious for the second stage decomposition, since the temperatures for Ln-NH<sub>4</sub> are 20°C lower than those for Ln-Rb. This difference is apparently due to the acceleration of the decomposition reaction caused by the heat evolved in the air atmosphere. The weight loss data seem to be in good agreement with the values calculated for probable losses of the water and the substance related to the ligand NH<sub>3</sub>. In order to characterize the intermediates formed by the first stage decomposition, samples of La-NH<sub>4</sub> and La-Rb were heated using the DTA-TG apparatus until the TG curves reached the first plateau. The samples were immediately removed and their IR spectra and X-ray diffraction patterns measured. The powder patterns showed that the intermediates from La-NH<sub>4</sub> and from La-Rb were isostructural, though the former still contained one remaining water molecule. As mentioned earlier, the hydrated complexes are also very similar in their structures. Therefore, we can conclude that one of three water molecules of Ln-NH<sub>4</sub> exists in a fairly different environment; this is undoubtedly related to the structural difference between NH<sub>4</sub><sup>+</sup> and Rb<sup>+</sup>. On dehydration, the characteristic splitting of the IR absorption bands around 1100 cm<sup>-1</sup> ( $\nu_3$ ) and 600 cm<sup>-1</sup> ( $\nu_4$ ) became more pronounced. This indicates that the sulfate ions gained more bidentate character than in the original lattice, where some of the water molecules would be occupying the coordination sites of the cation.

When La-NH<sub>4</sub> and La-Rb were heated at 280°C, the constant weights corresponding to plateau II were attained in the air flow, but in the Ar flow the weights decreased slowly over the points which corresponded to II. This indicates that further decomposition of the intermediates has already started at this temperature.

According to the discussion given so far, the decomposition of each

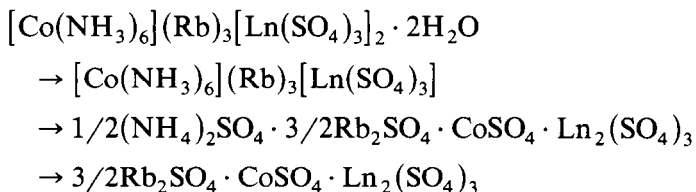
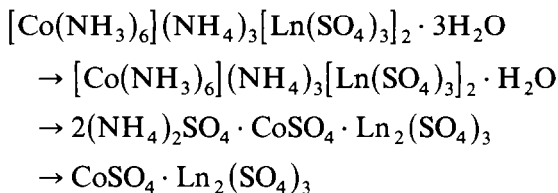
TABLE 2  
Peak temperatures and the weight losses due to the first (I) and the second (II) stage decompositions

Complex	In air		In Ar				Calcd. wt. loss $\Delta W$ (%)		
	I		II		I		II <sup>b</sup>		
	$T$ ( $^{\circ}\text{C}$ )	$\Delta W$ (%)	$T$ ( $^{\circ}\text{C}$ )	$\Delta W$ (%)	$T$ ( $^{\circ}\text{C}$ )	$\Delta W$ (%)	I <sup>a</sup>	II <sup>b</sup>	
La-NH <sub>4</sub>	220	3.25	313	8.26	223	3.54	338	3.21	9.09
Ce-NH <sub>4</sub>	219	3.62	289	8.05	220	3.86	322	3.20	9.07
Pr-NH <sub>4</sub>	222	3.28	308	8.42	224	3.48	337	3.20	9.05
La-Rb	204	2.91	309	6.79	207	3.21	336	2.76	6.43
Ce-Rb	203	3.01	308	6.83	204	3.49	323	2.75	6.42

<sup>a</sup> Calculated as a loss of 2H<sub>2</sub>O.

<sup>b</sup> Calculated as a loss of H<sub>2</sub>O + 4NH<sub>3</sub> + NH<sub>2</sub><sup>-</sup> for Ln-NH<sub>4</sub> and as that of 4NH<sub>3</sub> + NH<sub>2</sub><sup>-</sup> for Ln-Rb.

complex will give the stoichiometrically possible products as shown in the following schemes, which will be the same either in the air flow or in the Ar gas flow.



From the X-ray diffraction study of the intermediates, formation of any one of  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{Co}^{2+}$  or  $\text{Ln}^{3+}$  sulfates was not confirmed. Relatively large crystals of the complexes were heated, without being crushed, to  $280^\circ\text{C}$  in the air and in the Ar gas flow. Microscopic observation of the products showed that their original external shapes were retained and that they were transparent.

The most characteristic aspect of the thermal decomposition of these complexes is that the deamination reaction is exothermic in the air atmosphere, whereas it is endothermic in the inert atmosphere as is the case for the Nd(III) complexes, as already reported in a previous paper [1]. To analyse the evolved gas, the complexes were heated from room temperature to  $280^\circ\text{C}$  and held at that temperature for 1 h. The ammonia evolved in the stream of air or Ar was collected in a standard solution of hydrochloric acid. The percentages of the evolved fraction compared with the total ammonia coordinating to Co(III) were determined by titrating the remaining acid with a standard NaOH solution. The results are given in Table 3. Very small fractions were found in the air; however 70% was liberated in the Ar gas flow. As discussed before, it is certain that the product of the second decomposition contains  $\text{NH}_4^+$  originating from  $\text{NH}_3$ , because the reduction of Co(III) has been completed at this stage. Consequently, the fraction of  $\text{NH}_3$  liberated will not be larger than 5/6. The experimental results apparently show this to be the case. The relation between the fraction of  $\text{NH}_3$ , the atmosphere and the nature of the thermal effect is analogous to that for the Nd(III) complexes. Therefore, the same conclusion, that the deamination in air is accompanied by oxidation with atmospheric oxygen will also be reached here. By the simple peak area method the heats were estimated for the exotherm or the endotherm due to the second stage decomposition. The results are expressed in kJ per formula weight of the complexes and are given in Table 3. It is apparent that there is little difference between the

TABLE 3

Heats ( $q$ ) and fractions of evolved  $\text{NH}_3$  at the second stage decomposition

Complex	In air		In Ar	
	$q$ (kJ)	$\text{NH}_3$ (%)	$q$ (kJ)	$\text{NH}_3$ (%)
La-NH <sub>4</sub>	-1500	0.78	810	69.7
Ce-NH <sub>4</sub>	-1700	<1	730	76.2
Pr-NH <sub>4</sub>	-1600	2.1	730	76.4
La-Rb	-1600	0.27	600	70.2
Ce-Rb	-1500	0.82	670	73.7

values for various complexes as long as the atmosphere is the same. However these values are almost twice as large as those found for the Nd(III) complexes, either for the exotherm or for the endotherm. If we consider the heat evolving process to be the same as that proposed for the Nd(III) complexes, the values should be similar, because one formula weight of each complex contains a mole of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation which will be principally involved in the heat evolving or absorbing processes.

One reason for this large discrepancy will be found in the method of estimation itself. As seen in Fig. 1 the exotherms are extremely sharp and simple in shape. Compared with this, both TG and DTA curves for the Nd(III) complexes are rather complicated. This means that the process(es) in the complexes concerned here occur more rapidly than in the Nd(III) complexes, and thus the heat change is efficiently recorded as peaks with larger area. Because of this, the heats for the Nd(III) complexes might be underestimated.

The second stage decomposition may include the following processes: (i) the reduction of Co(III) to Co(II); (ii) the dissociation of the ammines; (iii) the formation of  $\text{NH}_4^+$  ion from the ligand ammonia; and (iv) the modifications of the cations and sulfate ions to the product phase. It is quite reasonable to regard the ligand ammonia, not the sulfate ion, as the reducing agent for Co(III) [2]. In the Ar gas flow, most of the ligand  $\text{NH}_3$  is liberated as a gaseous product in process (ii) and primarily causes the heat absorption. In the air flow, however, process (ii) means oxidative deamination, which involves atmospheric oxygen and transforms  $\text{NH}_3$  to  $\text{N}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  with the evolution of a large amount of heat. Thus this exothermic process must be described as being composed of many steps, the details of which are still not clear at present. However, the present study found that  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$ , if they are contained, do not participate in the exothermic decomposition, since there is no difference in the behavior of Ln-NH<sub>4</sub> and Ln-Rb. The formation of  $\text{NH}_4^+$  was supposed to compensate for the decrease in the cationic charge due to process (i), and was confirmed by the IR spectra of the products.



In a previous study [1], we reported that the simple sulfate  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and one of the Nd(III) complexes decomposed via the endothermic reaction even in the air atmosphere. In order to examine the specificity of such decomposition behavior, other ammine complexes of Co(III) such as aquapentaamminecobalt(III) sulfate  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , its Nd(III) complex,  $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Nd}(\text{SO}_4)_3] \cdot n\text{H}_2\text{O}$  and the Ce(IV) sulfato complex,  $[\text{Co}(\text{NH}_3)_6]_2[\text{Ce}(\text{SO}_4)_5] \cdot 5\text{H}_2\text{O}$  [6], were prepared. The DTA-TG measurements of these complexes, taken under the same conditions showed that the corresponding decomposition reaction of the first complex is endothermic and those of the other two are exothermic in the air atmosphere. Considering all the data together, it can be said that the Co(III) ammine complexes which contain sulfate ions coordinating to metal cations undergo exothermic deamination at about  $300^\circ\text{C}$  in the air atmosphere, suggesting that the sulfate ions are involved in the process in some way, although gaseous products containing sulfur have not been found in the stream of atmospheric gases.

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