Double sulphates of rare earths(III) with trimethylammonium.
Part 2. Synthesis and thermal decomposition of $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$

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(Received 12 April 1991)

Abstract

Double sulphates of rare earths(III) with trimethylammonium (Tr) were synthesised in molar ratio 1:20. Their thermal behaviour in dynamic conditions in the temperature interval 20–700°C were studied by TG, DTG and DTA. From the TG curves and quantitative analyses of rare earths and sulphate groups, their general empirical formula was found to be $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$, where Ln = Ce–Er and Y. Their thermal decomposition is also described.

INTRODUCTION

There are few data concerning double sulphates of M(III) with monovalent cations of stoichiometry $M_3Tr(SO_4)_3$. It is known that, in addition to $NH_4Sc(SO_4)_2$, Sc(III) with ammonium gives a compound with an empirical formula of $(NH_4)_3Sc(SO_4)_3$, established from its crystal structure [1]. It is also known that Ga(III), Cr(III), V(III), Fe(III) and Rh(III) with Ag(I) give two types of compounds: $AgTr(SO_4)_2$ and $Ag_3Tr(SO_4)_3$. It has been established that there is a difference in their crystal structure and an analogy with the crystal structure of the corresponding compounds of Na(I) [2]. Double sulphates of rare earths(III) with potassium of general empirical formula $K_3Ln(SO_4)_3$, have also been prepared and the parameters of the elemental cells determined [3]. In addition, double sulphates of Cs and Rb with the same general formula have been prepared and the parameters of their elemental cells determined [4].

As a continuation of our work on double sulphates of rare earths with trimethylammonium, this paper presents the results of investigations into the thermal decomposition of double sulphates of rare earths(III) with trimethylammonium of general empirical formula $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot$

4.5H$_2$O, obtained with molar ratios higher than 1:15 of rare earth(III) sulphate and trimethylammonium sulphate.

EXPERIMENTAL

The procedure for synthesis of double sulphates of rare earths(III) with trimethylammonium is given in Part I of this study (the previous paper in this issue). At molar ratio 1:20, double sulphates are obtained whose stoichiometry, established by means of quantitative analyses and TG thermal decomposition curves, is different from those of the double sulphates discussed in Part 1. The same thermoanalytical methods and experimental conditions were used as for examination of the rare earth double sulphates of general empirical formula (CH$_3$)$_3$NHLn(SO$_4$)$_2$·3H$_2$O, as described in Part 1.

RESULTS AND DISCUSSION

From X-ray powder diffraction patterns, it was established that all the double sulphates examined are isostructural. Their general empirical for-

TABLE 1

The results of thermal analyses of [(CH$_3$)$_3$NH]$_3$Ln(SO$_4$)$_3$·4.5H$_2$O

Ln (M_r) [a]		% H$_2$O	% Ln$_2$(SO$_4$)$_3$	% [(CH$_3$)$_3$NH]$_2$SO$_4$
Ce (689.72)	calcd.	11.75	41.21	47.04
	found	12.00	45.24	42.76
Pr (690.51)	calcd.	11.74	41.27	46.99
	found	11.76	41.52	46.72
Nd (693.84)	calcd.	11.68	41.55	46.76
	found	11.84	42.24	45.92
Sm (700.00)	calcd.	11.58	42.07	46.35
	found	12.05	42.45	45.50
Eu (701.56)	calcd.	11.56	42.20	46.25
	found	11.60	44.29	44.11
Gd (706.85)	calcd.	11.47	42.63	45.90
	found	12.35	42.80	44.85
Tb (708.53)	calcd.	11.44	42.77	45.79
	found	11.50	44.04	44.46
Dy (712.10)	calcd.	11.38	43.05	45.56
	found	11.50	44.40	44.10
Ho (714.53)	calcd.	11.35	43.25	45.41
	found	11.40	44.54	44.06
Er (716.86)	calcd.	11.31	43.43	45.26
	found	11.50	44.47	44.03
Y (638.51)	calcd.	12.70	36.49	50.81
	found	13.00	38.33	48.67

[a] M_r, relative molecular mass.
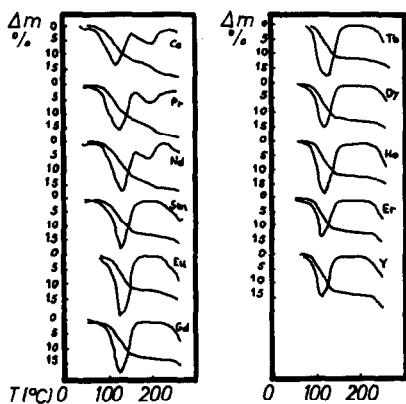
Fig. 1. TG and DTG curves of the dehydration of $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$.

mula was determined from the TG curves and from quantitative analyses of Ln and the sulphate group (Table 1). Quantitative analysis of the praseodymium compound, gave Pr, 19.93%, and the sulphate group 42.51% (calculated values, 20.41% and 41.73% respectively). As can be seen from the figures, their thermal decomposition is more complicated than those of the double sulphates of groups 1 and 2 (Part 1). Moreover, it is possible to resolve two stages of thermal decomposition. In the first stage, dehydration of the crystallohydrates takes place in one step (Fig. 1), beginning at about 40 °C and ending at temperatures below 170 °C, this can be expressed as

$$[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O(s) \rightarrow [(CH_3)_3NH]_3Ln(SO_4)_3 + 4.5H_2O(g)$$
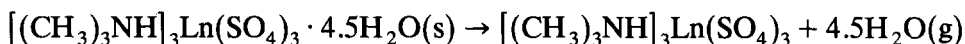
The second thermal decomposition stage (Fig. 2) begins above 160 °C for the cerium praseodymium and neodymium compounds. Because stage 2 of the thermal decomposition begins at such a low temperature, it is very difficult to resolve this stage from the first one. For the other compounds of this group, thermal decomposition of anhydrous double sulphate begins at temperatures higher than 220 °C and here two stages of thermal decomposition are well resolved. The second stage ends at about 450 °C (dysprosium and yttrium), 500 °C (neodymium), 550 °C (cerium, samarium, europium and gadolinium) and at 600 °C (terbium, holmium and erbium). If the temperatures of the beginning of thermal decomposition are compared with the temperature of the thermal decomposition of trimethylammonium sulphate in air (Fig. 3), because of the lower temperature of its decomposition in double sulphates, it can be concluded that trimethylammonium sulphate is destabilised in double sulphates. This stage of thermal decomposition of the double salts is associated with many exothermic maxima and, possibly, with formation of intermediate products. Therefore, step 1 of this stage can be attributed to the liberation of 1/3 of the trimethylamine and step 2 to the loss of the other 2/3 of the trimeth-
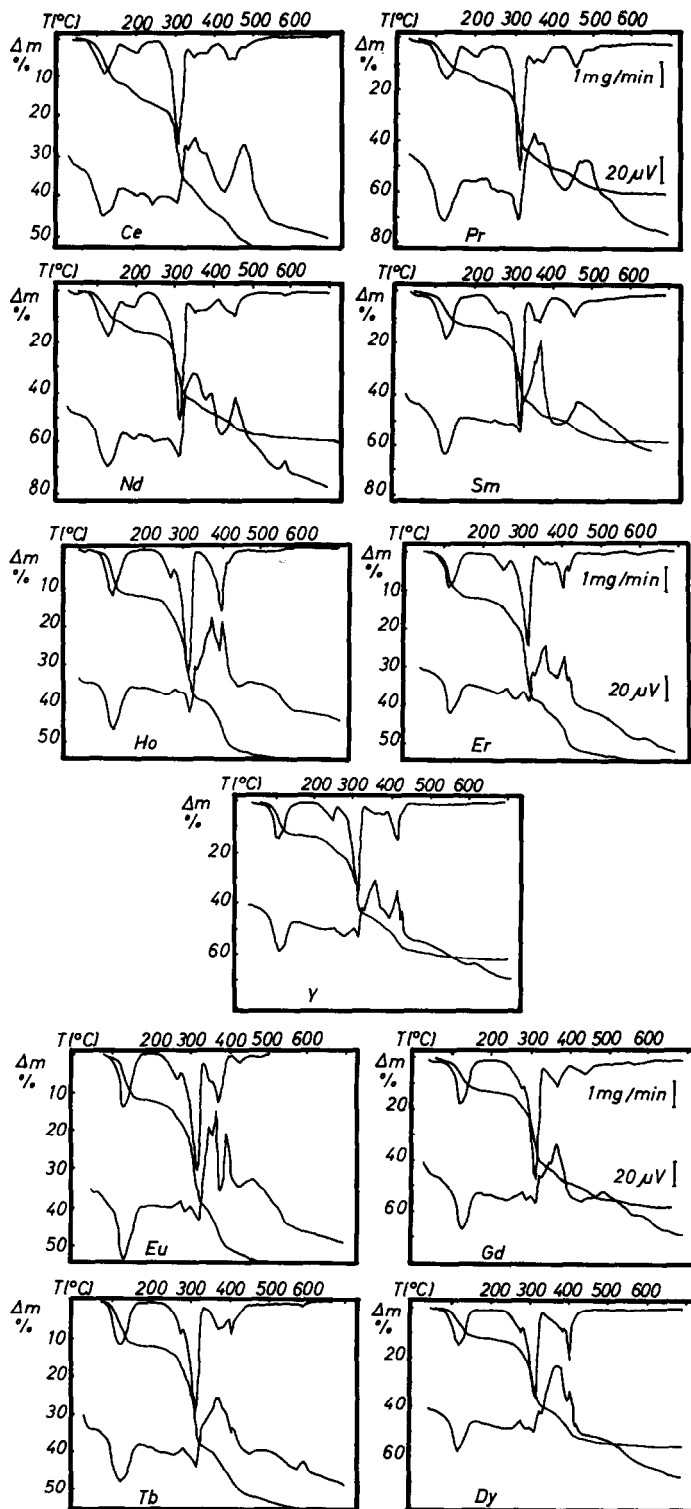
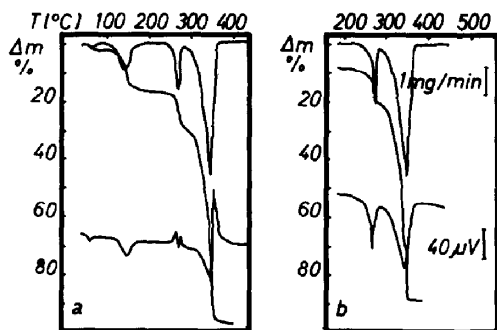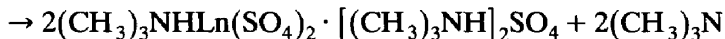Fig. 2. TG, DTG and DTA curves of the thermal decomposition of $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$.

Fig. 3. TG, DTG and DTA curves of the thermal decomposition of trimethylammonium sulphate: a, in air; b, in argon.

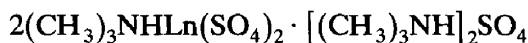ylamine; in step 3, sulphuric acid decomposes and evolves as $H_2O(g)$ and $SO_3(g)$:

1st step

$$2[(CH_3)_3NH]_3Ln(SO_4)_3$$
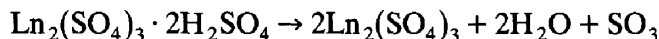$$\rightarrow 2(CH_3)_3NHLn(SO_4)_2 \cdot [(CH_3)_3NH]_2SO_4 + 2(CH_3)_3N$$

The calculated value for mass loss of the cerium compound is 8.55%; found from the TG curve, 6.7%.

2nd step

$$2(CH_3)_3NHLn(SO_4)_2 \cdot [(CH_3)_3NH]_2SO_4$$
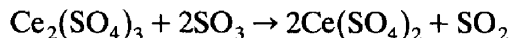$$\rightarrow 4(CH_3)_3N(g) + Ln_2(SO_4)_3 \cdot 2H_2SO_4$$

The calculated value for mass loss for the cerium compound is 17.1%; found from the TG curve, 18%.

3rd step

$$Ln_2(SO_4)_3 \cdot 2H_2SO_4 \rightarrow 2Ln_2(SO_4)_3 + 2H_2O + SO_3$$

For the cerium compound, this step includes an oxidation reaction of Ce(III) to Ce(IV) with some of the liberated SO_3 (not reduced with liberated carbon) as follows:

$$Ce_2(SO_4)_3 + 2SO_3 \rightarrow 2Ce(SO_4)_2 + SO_2$$

This reaction is associated with an exothermic maximum at about 475°C. The calculated value for $Ce(SO_4)_2$ as residue is 48.25%; found from the TG curve, 45.24%.

The first step of the second stage of the thermal decomposition is well resolved for compounds of Ce, Pr and Nd, but for Sm, Eu, Gd, Tb, Dy, Ho, Er and Y, it is very close to the second step. Nor is step 3 of stage 2 well resolved from step 2.

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