

# Synthesis and thermal decomposition of some rare earth(III) dimethylammonium sulphate crystallohydrates. Part 2. Results of investigations of $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$

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(Received 29 September 1992)

## Abstract

Double sulphates of rare earths(III) with dimethylammonium were obtained by evaporation of aqueous reaction mixtures of rare earth(III) sulphates and dimethylammonium sulphate in molar ratios greater than 1:20. By means of X-ray powder diffraction patterns, it was found that they are isostructural. From the TG curve of the thermal decompositions of the obtained compounds in the temperature interval from 20 to 700°C, their general empirical formula was established as  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  (where Ln is Nd, Sm, Eu, Gd, Tb).

The thermal decomposition of the anhydrous double salts takes place with thermal effects on the DTA curve, which means that this process is not a simple dissociation, but that intermediate products are possibly involved. The equations of the thermal decomposition are also presented.

## INTRODUCTION

There are few data concerning double sulphate crystallohydrates of M(III) with monovalent cations having a stoichiometry greater than 1:1. The crystalline structures double sulphates of general empirical formula  $\text{K}_6\text{Ln}_4(\text{SO}_4)_9 \cdot 8\text{H}_2\text{O}$  (where Ln is Ce–Gd) and  $\text{Na}_3\text{Sc}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  have been published [1]. Recently, the results of the synthesis and thermal decomposition of  $(\text{CH}_3)_3\text{NHTr}(\text{SO}_4)_3 \cdot 4.5\text{H}_2\text{O}$  (where Tr is Ce–Er and Y) have been presented [2]. We also have data on the synthesis and thermal decomposition of  $[(\text{CH}_3)_4\text{N}]_4\text{Ln}_2(\text{SO}_4)_5 \cdot 10\text{H}_2\text{O}$  (where Ln is Ce and Pr) (to be published).

There is plenty of data on the anhydrous double sulphates of M(III) with different monovalent cations. They are obtained from aqueous solutions or from solid–solid reactions. Thus, the double sulphates  $\text{M}(\text{I})_3\text{M}(\text{III})(\text{SO}_4)_3$

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(where M(I) is K, M(III) is La–Nd; M(I) is Cs, M(III) is La, Yb, Gd),  $M(I)_3Sc(SO_4)_3$  and  $M(I)_4Ln_2(SO_4)_5$  (where M(I) is K and Rb and M(III) is rare earth),  $M(I)_5M(III)(SO_4)_4$  (where M(I) is K, Rb or  $NH_4$ ),  $K_8Ln_2(SO_4)_7$ ,  $K_6Y_4(SO_4)_9$  and  $K_6Ln_4(SO_4)_9$ , have been investigated [1]. It was found that they crystallize with low symmetry and that the type of stoichiometry depends on the ionic radii of M(I) and M(III). Double sulphates with Li(I) of higher stoichiometry are not known. It has also been established that double sulphates with stoichiometry higher than 1:1 are less stable.

As a continuation of our work on double sulphates of rare earths with dimethylammonium, this paper deals with the results of the investigations into the thermal decomposition of double sulphates of rare earths(III) with dimethylammonium, of general empirical formula  $[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$  (where Ln is Nd–Tb), obtained with molar ratios of rare earth(III) sulphate and dimethylammonium sulphate of higher than 1:20.

## EXPERIMENTAL

The procedure for synthesis of double sulphates of rare earths(III) with dimethylammonium is given in Part 1 of this study [3]. The stoichiometry of the obtained compounds has been established from the TG curves of the thermal decomposition and on the basis of the isostructurality of these compounds. The same thermoanalytical methods and experimental conditions were used as for the compounds presented in Part 1.

## RESULTS AND DISCUSSION

With molar ratios higher than 1:20, double sulphates of general empirical formula  $[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$  (where Ln is Nd–Tb) were obtained (for analyses, see Table 1). On the basis of their X-ray powder diffraction patterns, it has been concluded that the above compounds are isostructural. Their general empirical formula has been

TABLE 1

Results of the thermal analysis of double sulphates of general empirical formula  $[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$

Ln (Mr)	H <sub>2</sub> O in %	Ln <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> in %	$[(CH_3)_2NH_2]_2SO_4$ in %
Nd (624.74)	8.25(8.65)	47.45(46.15)	44.30(45.20)
Sm (630.85)	8.11(8.58)	48.55(46.68)	43.34(44.76)
Eu (632.46)	9.13(8.55)	46.72(46.81)	44.07(44.64)
Gd (637.75)	8.32(8.48)	48.30(47.25)	43.68(44.28)
Tb (639.42)	8.13(8.45)	48.34(47.39)	43.52(44.16)

Theoretical values are given in parentheses.

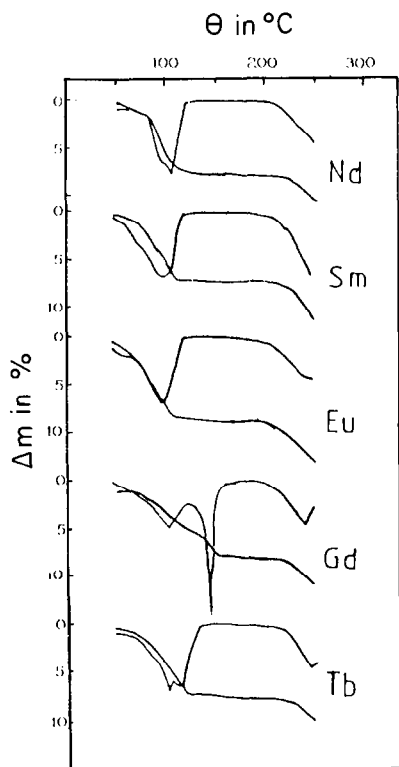


Fig. 1. TG and DTG curves of the dehydration of  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ .

constructed from their thermal decomposition. The final product  $\text{Ln}_2(\text{SO}_4)_3$  was confirmed with X-ray powder diffraction patterns.

The thermal decomposition of the obtained double sulphates takes place in two well-resolved states (Fig. 2(a)–(e)). The TG, DTG and DTA curves are identical for all the investigated compounds. In the first stage (Fig. 1), the compounds lose their crystal water, this process taking place in one step or in two very closely related steps, an exception being the Gd compound where two steps are well resolved: it loses about two moles of water at about  $102^\circ\text{C}$  and the remaining mole at about  $140^\circ\text{C}$ . Table 2 shows that the DTG maxima of dehydration occur at temperatures of about  $100^\circ\text{C}$ ; those determined in Part 1 (Table 2) are higher. Hence, it can be concluded that the trihydrates are less stable. This conclusion corroborates the lower stability of the corresponding anhydrous double salts: the second stage of their thermal decomposition takes place at temperatures above  $200^\circ\text{C}$  (for the compounds in Part 1 [3], above  $300^\circ\text{C}$ ). The thermal decomposition of this stage is more complicated than that of pure dimethylammonium sulphate (see Fig. 3). At this stage which takes place with many thermal effects, the anhydrous double salts first lose one mole of dimethylammonium sulphate and in the second step, the remaining 0.5 mole of

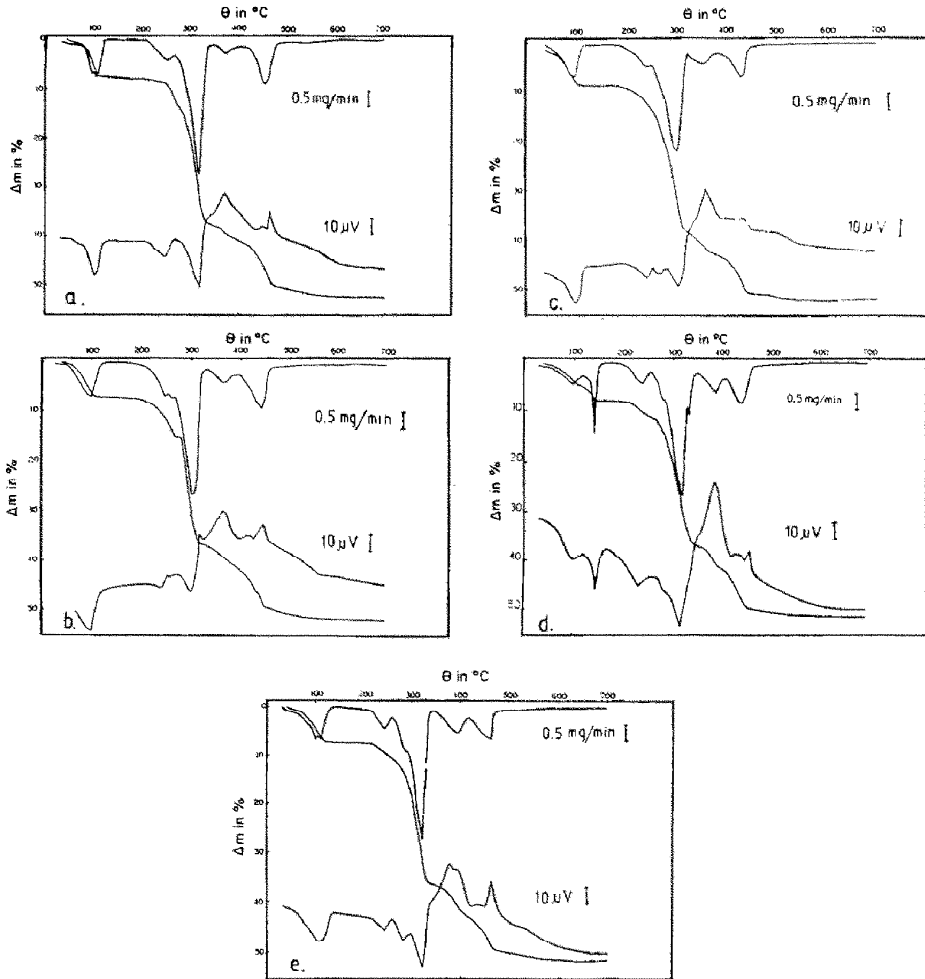


Fig. 2. TG, DTG and DTA curves of the thermal decomposition of  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$  (where Ln is Nd (a), Sm (b), Eu (c), Gd (d) and Tb (e)).

TABLE 2

DTG maxima of the thermal decomposition of  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$

Ln	$\theta/^\circ\text{C}$		
Nd	106	254	319, 376, 454
Sm	100	246	302, 442
Eu	97	250	300, 355, 442
Gd	102, 141	238	317, 390, 440
Tb	100, 115,	243	320, 395, 462

Note: DTG maxima ( $\theta/^\circ\text{C}$ ) of  $[(\text{CH}_3)_2\text{NH}_2]_2\text{SO}_4$ : in air, 264, 314, 318; and in argon, 276, 320.

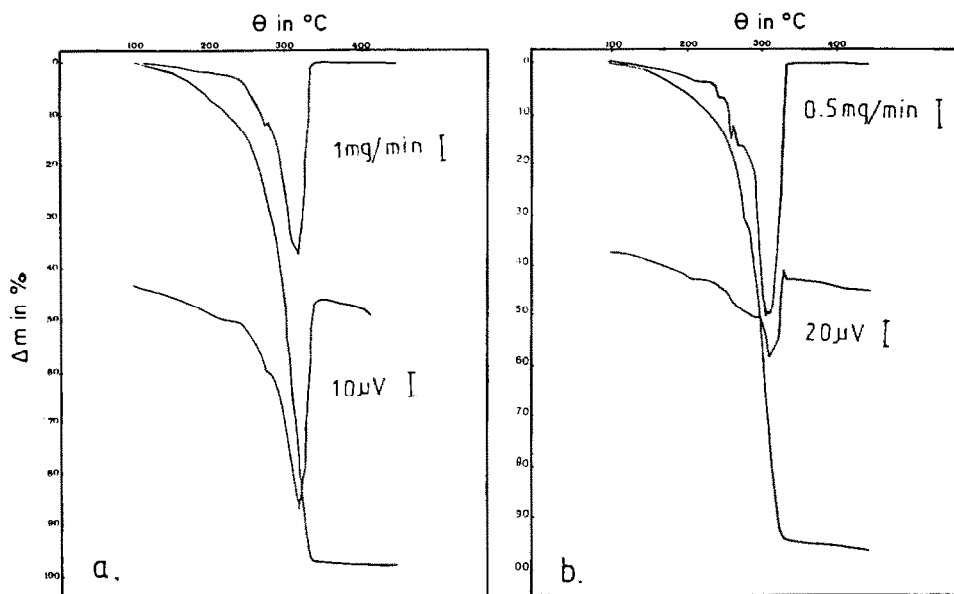
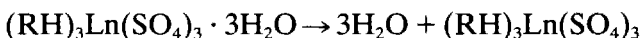


Fig. 3. TG and DTA curves of the thermal decomposition of dimethylammonium sulphate (a) in argon; (b) in air.

dimethylammonium sulphate is lost. This indicates that the resulting double sulphate is more stable than the initial double sulphate. The thermal decomposition of these compounds can be expressed in the equations (where R is  $(\text{CH}_2)_2\text{NH}$ )

1st stage



2nd stage

1st step



Mass losses in % for compounds of Nd, 29.25 (30.11); Sm, 32.59 (29.83); Eu, 32.10 (29.75); Gd, 28.95 (29.50); Tb, 29.87 (29.43).

2nd step



Mass losses in % for compounds of Nd, 15.05 (15.05); Sm, 10.75 (14.91); Eu, 11.97 (14.88); Gd, 14.73 (14.75); Tb, 13.65 (14.71).

(R =  $(\text{CH}_3)_2\text{NH}$ )

Theoretical values are given in parentheses.

## ACKNOWLEDGEMENT

Financial support by the Research Community of Slovenia is gratefully acknowledged.

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