

Synthesis and thermal decomposition of some rare earth(III) dimethylammonium sulphate crystallohydrates. Part 1. Results of investigations of $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (where Ln is La–Gd)

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Abstract

The double sulphates of some rare earths(III) with dimethylammonium were obtained as crystalline products by evaporation at room temperature of an aqueous mixture of Ln(III) sulphate and dimethylammonium sulphate in molar ratio from 1:4 to 1:15, and treatment, in some cases, of the concentrated mixture with ethanol. The identification was carried out by means of X-ray powder diffraction patterns. It was found that they are isostructural. On the basis of the thermal decomposition and chemical analysis of the obtained double salts, their general empirical formula $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ was established. It was found that rare earth(III) sulphates are obtained at 700°C. The thermal decomposition takes place in two well-resolved stages. The decomposition of the anhydrous double salts is not a simple dissociation, but involves intermediate reactions.

INTRODUCTION

Double sulphates of rare earths with classical monovalent cations and ammonium have been the subject of many investigations [1, 2]. The thermal decomposition of some double sulphates of rare earths were studied by Zajceva et al. [3], Ishakova et al. [4] and Bukovec et al. [5]. There is also some data on double sulphates of rare earths with alkylammonium cations. The results of the synthesis and thermal decomposition of double sulphates of rare earths with methylammonium [6], dimethylammonium [7], trimethylammonium [8, 9] and tetramethylammonium [10] have recently been presented. The differences in the thermal decomposition in air and in inert atmosphere of some of the above double sulphates have also been investigated [11].

The crystal structures of $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (where Ln is Tb, Dy, Ho, Er, Tm, Yb and Y) [12] and $(\text{CH}_3)_4\text{NCe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ [13] have

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also been studied. It was found that in these double sulphates, Ln is coordinated with 8 oxygen atoms.

As a part of our investigation of the salts and double salts of rare earths, two other series, besides that presented in ref. 7, of double sulphates of rare earths with dimethylammonium, of general empirical formula $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (where Ln is La–Gd) and $[(\text{CH}_3)_2\text{NH}_2]_3\text{Ln}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ (where Ln is Nd–Tb) were prepared and investigated using chemical analyses, X-ray powder diffraction patterns, and thermogravimetry, derivative thermogravimetry and differential thermal analysis. Part 1 of this work presents the results for the double sulphate monohydrates, and Part 2 the results for the double sulphate trihydrates.

The X-ray powder diffraction patterns used for identification of the products are not presented here.

EXPERIMENTAL

Procedure and methods

The double sulphates of rare earths(III) and dimethylammonium were obtained by evaporation at room temperature of an aqueous mixture of rare earth(III) sulphates and dimethylammonium sulphate in molar ratio from 1:4 to 1:20, and by subsequent treatment of some concentrated reaction mixtures with ethanol. The crystal substances obtained were filtered off, washed with aqueous ethanol and dried in air. For other details of the starting materials, please refer to ref. 7. The products were identified as new compounds by their X-ray powder diffraction patterns. The obtained double sulphates were studied by means of TG, DTG and DTA and, for some, by chemical analyses of Ln(III) and SO_4^{2-} group.

The thermoanalytical curves were obtained on a Mettler thermoanalyser in dynamic dry air (flow rate 5 l h^{-1}), using a Pt/Pt–Rh thermocouple and Pt crucibles (TD1). The sample mass was approximately 100 mg, and the heating rate was 6°C min^{-1} . The reference material for the DTA determinations was $\alpha\text{-Al}_2\text{O}_3$ in the range 20–700°C.

RESULTS AND DISCUSSION

As has already been determined [7], two different isostructural groups are formed when the reactants are in molar ratio from 1:4 to 1:15: one with a general empirical formula $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ with the lighter lanthanides from La to Gd, and another $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ with the heavier lanthanides from Tb to Lu and Y. Here we present the results of the investigation of the first isostructural group (for analyses, see Table 1).

The thermal decomposition of double sulphates of this group can be divided into mainly two stages. In the first stage, dehydration of the

TABLE 1

Results of thermal analysis of double sulphates of rare earths(III) with dimethylammonium of general empirical formula $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

Ln (Mr)	H ₂ O in %	Ln ₂ (SO ₄) ₃ in %	[(CH ₃) ₂ NH ₂] ₂ SO ₄ in %
La (395.13)	5.63(4.56)	69.00(71.62)	25.37(23.82)
Ce (396.34)	4.80(4.55)	71.44(71.71)	23.76(23.74)
Pr (397.13)	4.90(4.54)	70.90(71.76)	24.20(23.70)
Nd (400.46)	5.50(4.50)	70.24(72.00)	24.26(23.50)
Sm (406.62)	4.87(4.43)	72.40(72.42)	22.73(23.15)
Eu (408.18)	4.91(4.40)	72.07(72.53)	23.02(23.06)
Gd (413.47)	4.40(4.36)	72.77(72.88)	22.83(22.76)

The theoretical values are given in parentheses.

Note: The values for the chemical analyses of Pr(III) and SO₄²⁻ group of the Pr double salt are 35.15 (35.48)% and 47.46 (48.38)%.

monohydrates takes place and in the second, the decomposition of the anhydrous double salts. As can be seen from Fig. 1, the dehydration takes place above 100°C. The temperature of the DTG maxima (Table 2) increases from the La to Sm compounds, but decreases from the Eu to Gd compounds. This means that with the reduction of the ionic radius of Ln(III) (a lanthanide ionic contraction [14]), the stability of the monohydrates increases up to the Sm compound, after which the opposite tendency appears.

The second stage of the thermal decomposition is very complex and takes place with many thermal effects (see Fig. 2(a)–(g)). The exothermic

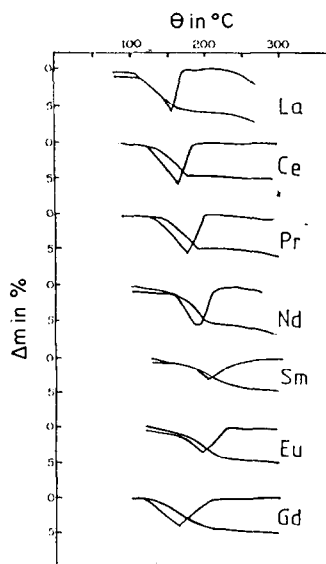


Fig. 1. TG and DTG curves of the dehydration of $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$.

TABLE 2

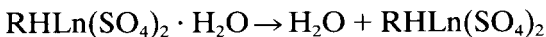
DTG maxima of the thermal decomposition of $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, see Fig. 2(a)–(g)

Ln	$\theta/^\circ\text{C}$		
La	157	270	385, 430
Ce	167		359, 394, 448
Pr	177		352, 394, 439
Nd	191	297	356, 396, 430, 441
Sm	210		364, 400, 442
Eu	196		365, 376, 432
Gd	165		346, 374, 423

effects indicate that this process is not a simple thermal dissociation, but that intermediate reactions and transformations can be assumed to take place. On the basis of the total mass losses, which are in agreement with the theoretical values if lanthan(III) sulphate is obtained (Table 1), it is proposed that the final product formed at 700°C is lanthan(III) sulphate. Some larger deviations from the obtained values, seen for the Ln and Nd compounds, can be attributed to the presence of moisture and occluded unreacted dimethylammonium sulphate in the isolated compounds (concluded from Fig. 2(a) and (d), where DTG maxima appear on the DTG curves at 270 and 287°C , see also Table 2), related to a mass loss on the TG curve of about 1.5%.

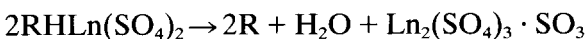
Part 2 of this research (fig. 3(a) and (b)) [16] shows that the thermal decomposition of pure dimethylammonium sulphate begins at about 200°C and the highest intensity is reached at about 300°C ; but with the double sulphates, decomposition begins above 300°C and peaks at about 470°C (see Table 2). This means that the double salts of dimethylammonium sulphate are stabilized with an additional bonding. This is also noticed in other double sulphates [10, 15]. From the TG curve, it can be inferred that at this stage the anhydrous double salt loses dimethylamine and water in the first step and sulphur trioxide in the second. On the basis of the mass losses (TG curves), the thermal decomposition of the investigated compounds occurs according to the equations (where R is $(\text{CH}_2)_2\text{NH}$)

1st stage



2nd stage

1st step



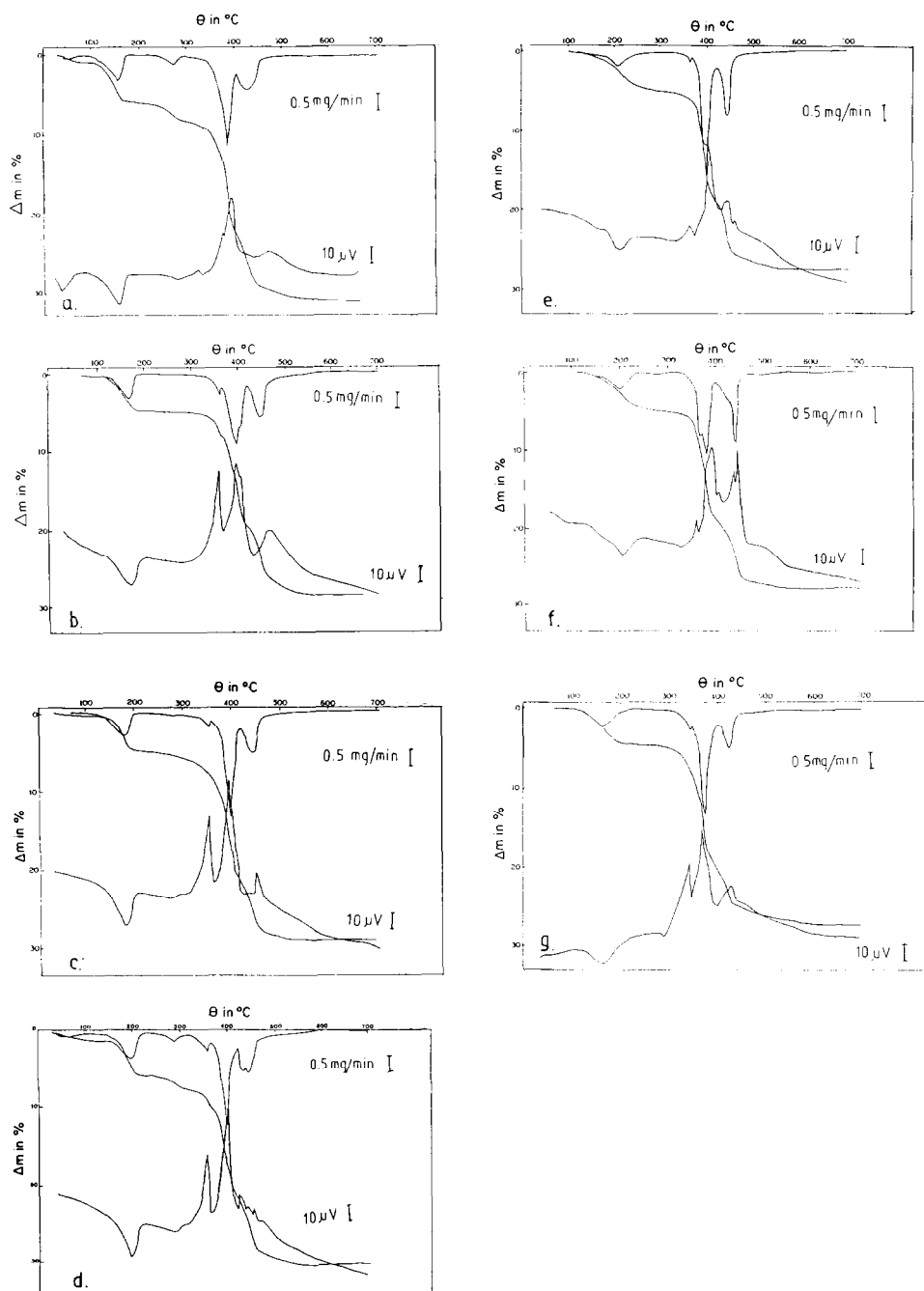
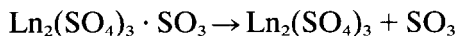


Fig. 2. TG, DTG and DTA curves of the thermal decomposition of $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ where Ln is La (a), Ce (b), Pr (c), Nd (d), Sm (e), Eu (f) and Gd (g).

Mass losses in % for compounds with La, 14.10 (13.69); Ce, 13.32 (13.63); Pr, 15.35 (13.62); Nd, 12.60 (13.50); Sm, 13.24 (13.30); Eu, 14.18 (13.24); Gd, 14.10 (13.08).

2nd step



Mass losses in % for compounds with La, 9.00 (10.12); Ce, 10.43 (10.09); Pr, 9.85 (10.07); Nd, 10.88 (9.98); Sm 9.49 (9.84); Eu, 9.85 (10.07); Gd, 8.73 (9.68).

The theoretical values are given in brackets.

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