

Double sulphates of rare earths(III) with trimethylammonium. Part 1. Synthesis and thermal behaviour of $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$

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Abstract

The double sulphates of some Ln(III) rare earths with trimethylammonium were obtained as crystalline products by evaporation at room temperature of an aqueous mixture of Ln(III) sulphate and trimethylammonium sulphate and treatment, in some cases, of the concentrated mixture with ethanol. After identification by means of X-ray powder diffraction patterns, it was found that three groups of double sulphates with different crystal structures were obtained. The results of the investigations of two groups with general empirical formula $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ are given. They were examined by means of TG, DTG and DTA analyses, from 20 to 700 °C. It was found that there is a difference in the thermal decomposition of these structurally different groups, in particular, a difference in the thermal decomposition of their anhydrous double sulphates.

1. INTRODUCTION

The double sulphates of monovalent alkali metal, Ti(I), ammonium or hydrazinium and trivalent rare earths, have been the subject of many investigations.

There are also some data for double salts of rare earths(III) with aliphatic ammonium ions. The synthesis, thermal behaviour and crystal structure of some double sulphates of rare earths(III) with dimethylammonium were recently presented [1,2]. An isomorphous series from Tb to Lu and Y with empirical formula $(\text{CH}_3)_2\text{NH}_2\text{Ln}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was found. It was found that they crystallize in the orthorhombic space group *Pnma* with 4 formula units in the unit cell. The difference in the thermal decomposition of some double sulphates of rare earths(III) with methylammonium(I) in air and in argon have also been presented [3]. It was found that thermal decomposition of the rare earth sulphate takes place at lower temperatures in argon than in air. The synthesis and thermal decomposition, as well as the determination of the stoichiometry of the double sulphates of some

rare earths(III) with monomethylammonium by means of TG curves, have also been reported [4]. The crystal structure of tetramethylammonium cerium(III) bis(sulphate) trihydrate was recently presented [5]. It was found that this compound crystallizes in the orthorhombic space group $Pca2_1$, with $Z = 4$.

As a continuation of the work on the synthesis of double sulphates of trivalent and monovalent cations, we present here the results of the synthesis, the chemical analyses and thermal analyses in dynamic conditions of double sulphates of some rare earths(III) with trimethylammonium(I). Because three groups of compounds with different crystal structures have been identified, Part 1 of this paper presents the results of investigations of the double sulphates of groups 1 and 2, with general empirical formula $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$; the results of investigations of group 3, with general empirical formula $[(\text{CH}_3)_3\text{NH}]_3\text{Ln}(\text{SO}_4)_3 \cdot 4.5\text{H}_2\text{O}$ are given in Part 2 (the next paper in this issue).

X-ray powder diffraction patterns for identification of the double sulphates are not presented here.

EXPERIMENTAL

Procedure and methods

The double sulphates of rare earths(III) and trimethylammonium were obtained by evaporation at room temperature of an aqueous mixture of rare earth(III) sulphate and trimethylammonium sulphate in molar ratio greater than 1:10 and up to 1:20, and by subsequent treatment of some concentrated reaction mixtures with ethanol. The obtained crystal substances were filtered off, washed with ethanol and dried in air. The crystal products were identified as new products by their X-ray powder diffraction patterns. The double sulphates were studied by means of TG, DTG and DTA. The thermoanalytical curves were obtained on a Mettler Thermoanalyser in dynamic dry air: flow rate 5 l h^{-1} ; Pt/Pt-Rh thermocouple; Pt crucibles (TD1); sample mass, approximately 100 mg; heating rate, $6^\circ \text{C min}^{-1}$; the reference for the DTA determinations was $\alpha\text{-Al}_2\text{O}_3$, in the temperature range from 20 to 700°C .

RESULTS AND DISCUSSION

From the X-ray powder diffraction patterns, it was possible to define three structurally different groups of double sulphates. Group 1 includes the double sulphates from La to Nd, and group 2, from Er to Lu, both obtained in a molar ratio of trimethylammonium sulphate and lanthanide sulphate from 10:1 to 15:1. Group 3 contains double sulphates from Ce to Er and Y, obtained in a molar ratio of about 20:1 and, as a second crystal

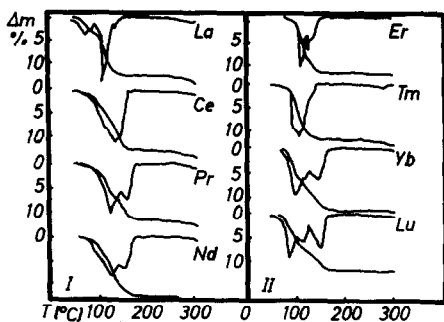


Fig. 1. TG and DTG curves of the dehydration of $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$.

fraction, in a 15:1 ratio. Using the TG curves and the results of quantitative analyses of the Ce and SO_4 group for trimethylammonium cerium(III) sulphate trihydrate (calculated value for Ce, 31.39%; found, 31.08%; and for the sulphate group, calculated value, 43.04%; found, 42.84%), the following general empirical formulae were found for the three groups

- Group 1, $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Ln = La–Nd)
 Group 2, $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Ln = Er–Lu)
 Group 3, $[(\text{CH}_3)_3\text{NH}]_3\text{Ln}(\text{SO}_4)_3 \cdot 4.5\text{H}_2\text{O}$ (Ln = Ce–Er and Y)

Because the stoichiometry of group 3 is quite different from those of groups 1 and 2, and because this group contains the double sulphates of 11 elements, it is more convenient to report the results of the thermal investigations of this group in Part 2 of this study.

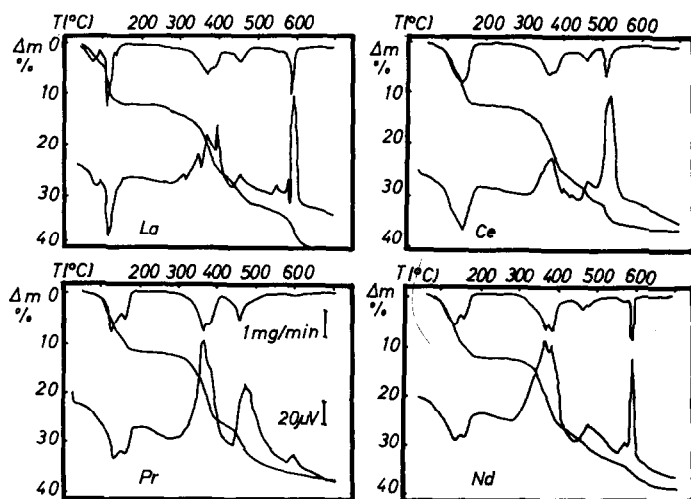


Fig. 2. TG, DTG and DTA curves of the thermal decomposition of $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, group 1.

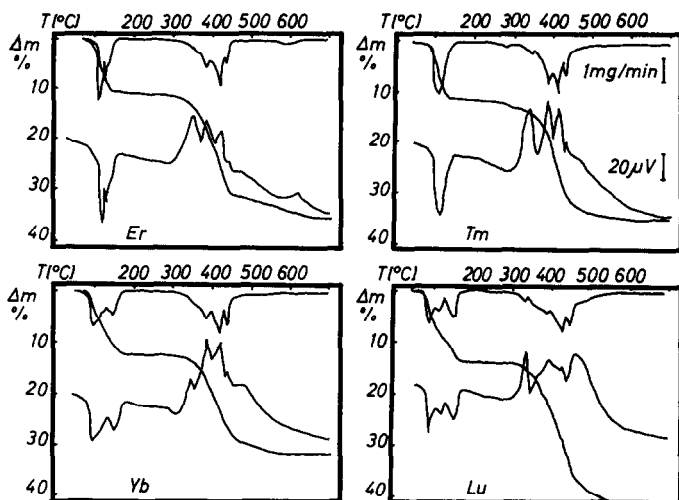
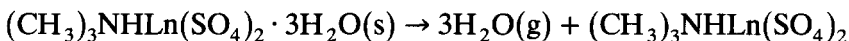


Fig. 3. TG, DTG and DTA curves of the thermal decomposition of $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, group 2.

From the TG, DTG and DTA curves (Figs. 1–3), it can be seen that the thermal decomposition is similar in each isomorphous group but that it is different between the groups. Figure 2 shows that the thermal decomposition of the double sulphates of group 1 takes place in two well-resolved stages. In the first stage, associated with the dehydration, the evolution of the water molecules occurs at different rates and two DTG maxima appear (an exception is the cerium compound where only one DTG maximum can be observed) (Fig. 1). The dehydration begins above 50°C and continues up to 160°C for La, 170°C for Ce and 180°C for Pr and Nd. The mass loss for this stage corresponds to 3 molecules of water (Table 1). This process can be expressed by the equation



The second stage of thermal decomposition which begins at about 280°C and ends at about 600°C , involves many steps; therefore, the thermal decomposition of anhydrous double sulphate is very complex and takes place with the formation of intermediate products. In the case of the lanthanum compound, the second stage of the thermal decomposition can be expressed as

1st step



The calculated value for mass loss as trimethylamine is 13.28%; obtained from TG curve, 13%.

2nd step



TABLE 1

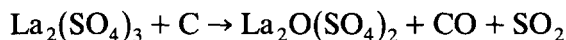
Thermal decomposition of double sulphates of rare earths with trimethylammonium, $(\text{CH}_3)_3\text{NHLn}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$

Ln (M_r) ^a		% H ₂ O	% Ln ₂ (SO ₄) ₃	% [(CH ₃) ₃ NH] ₂ SO ₄
Group 1				
La (445.19)	Calcd.	12.14	63.56	24.29
	Found	12.10	59.46	28.44
Ce (446.40)	Calcd.	12.11	63.67	24.23
	Found	12.17	63.70	24.13
Pr (447.19)	Calcd.	12.09	63.73	24.18
	Found	12.25	63.70	24.05
Nd (450.52)	Calcd.	12.00	64.00	24.00
	Found	12.20	61.42	26.38
Group 2				
Er (473.54)	Calcd.	11.41	65.75	22.84
	Found	11.50	65.40	23.10
Tm (475.22)	Calcd.	11.37	65.87	22.76
	Found	11.60	65.26	23.14
Yb (479.32)	Calcd.	11.28	66.16	22.56
	Found	12.42	67.89	19.69
Lu (481.25)	Calcd.	11.23	66.30	22.47
	Found	11.20	66.55	22.25

^a M_r , relative molecular mass

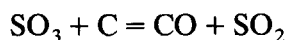
The calculated value for mass loss as sulphuric acid is 11.04%; obtained, 10.95%. In the final step, some of the lanthanum(III) sulphate is possibly decomposed in the presence of liberated carbon, i.e.

3rd step



The calculated residue as $\text{La}_2\text{O}(\text{SO}_4)_2$ is 54.56%; obtained, 59.46%. This step is connected with the exothermic maximum at 500 °C. The liberation of carbon can be confirmed from the thermal decomposition of trimethylammonium sulphate where the residue at 450 °C appears to contain a small amount of carbon.

The double sulphate of cerium decomposes in a similar way but in the third step of the second stage, only the reaction of SO_3 with liberated carbon takes place



with one exothermic maximum at 520 °C and cerium(III) sulphate as the final product.

In the thermal decomposition of the anhydrous double sulphate of praseodymium, only two steps can be distinguished in the second stage. In the first step, trimethylamine is evolved (calculated value, 13.22%; obtained from TG curve, 13.5%) and in the second step, one molecule of

sulphuric acid is lost. In this stage, exothermic maxima can be seen which means that this process is connected with formation of intermediate products. As a final product, $\text{Pr}_2(\text{SO}_4)_3$ is obtained.

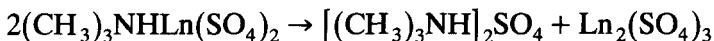
The second stage of the thermal decomposition of the anhydrous double sulphate of neodymium is similar to that of praseodymium, but one more step at about 500°C can be seen. This step can be attributed to partial decomposition of $\text{Nd}_2(\text{SO}_4)_3$ to $\text{Nd}_2\text{O}(\text{SO}_4)_2$ by means of liberated carbon, as for the lanthanum compound.

The thermal decomposition of the double sulphates of isomorphous group 2 takes place in two clearly separated stages (Fig. 3). In the first stage, at temperatures above 60°C , a dehydration process takes place. The loss of the water molecules proceeds at different rates and is connected with two or more endothermic effects. An exception is the thulium compound, where only one endothermic maximum appears and the dehydration takes place over a narrow temperature range (Fig. 1). The second stage of the thermal decomposition begins above 300°C and ends at about 450°C . This stage is connected with more exothermic effects; however, no more steps can be resolved on the TG curves.

It seems that the thermal decomposition of group 2 is different from that of group 1, possibly because of their different crystal structures. The thermal decomposition of the double sulphates of group 2 can be expressed:

1st stage, as for group 1;

2nd stage



Further exothermic peaks at this stage of the thermal decomposition suggest that intermediate products are obtained; but because they exist over a short temperature range, it was not possible to resolve more steps on the TG curves.

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