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# SYNTHESIS AND THERMAL DECOMPOSITION OF SOME RARE EARTH TETRAMETHYLAMMONIUM DOUBLE SULPHATES

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## Abstract

When reaction mixtures of rare earth(III) sulphates and tetramethylammonium sulphate in molar ratios of from 1:4 to 1:12 were evaporated at ambient temperature and the concentrated reaction mixture was treated with ethanol, double sulphates with general empirical formula $(CH_3)_4NLn(SO_4)_2{\cdot}2H_2O$ ($Ln$=Ho–Lu and Y) were obtained as reaction products. The crystalline products were identified by quantitative analysis, X-ray powder diffraction patterns and TG, DTG and DTA analysis. They were found to be isostructural. Their thermal decomposition took place in three stages. The temperature range of the dehydration mainly decreased from Ho to Lu. The thermal decomposition in the second and third stages occurred with many thermal events. As final product, $Ln_2O(SO_4)_2$ was obtained.

**Keywords:** rare earth tetramethylammonium double sulphates, TG-DTG-DTA, X-ray

## Introduction

Several double sulphates of rare earth(III) and monovalent cations such as Li(I), Na(I), K(I), Rb(I), Cs(I), Tl(I), $NH_4$(I) and $H_2NNH_3$(I) have been studied in detail previously. There have also been investigations on the double sulphates of rare earths(III) with monovalent alkylammonium cations [1–8]. The synthesis, thermal decomposition and crystal structure determination of rare earth double sulphates with dimethylammonium have recently been reported. It was found that the double sulphates with the general empirical formula $(CH_3)_2NH_2Ln(SO_4)_2{\cdot}4H_2O$ ($Ln$=Tb–Yb and Y) are isomorphous and crystallize in the orthorhombic space group Pnma with $Z=4$ [3]. The mechanism of their thermal decomposition was also presented [1]. The differences in thermal decomposition of some double sulphates of rare earths(III) with methylammonium(I) in an inert atmosphere and in air have also been reported [2]. It was found that the thermal decompositions of the double sulphates in an inert atmos-

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phere take place at lower temperature than in air. The synthesis of the double sulphates of rare earth with monomethylammonium, their thermal decomposition and determination of their stoichiometry by means of the TG curves have similarly been reported [8]. There are also data on the synthesis and thermal behaviour of the trimethylammonium rare earth double sulphates, and two types of compounds have been found [4, 5]: (1) one with the general empirical formula $(CH_3)_3NHLn(SO_4)_2 \cdot 3H_2O$ (in two different isomorphous groups, one from La to Nd and the other from Er to Lu) and (2) another type of isostructural, compounds with formula $[(CH_3)_3NH]_3Ln(SO_4)_3 \cdot 4.5H_2O$ (*Ln*=Ce–Er and Y).

On synthesis of the tetramethylammonium rare earth(III) double sulphates, two different structural groups have been obtained, one for *Ln*=Ce–Eu and the other for *Ln*=Gd–Dy, but with the same general empirical formula, $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$ [6]. Their thermal decompositions have also been studied. The crystal structure of the Ce compound, which belongs in the first isostructural groups, has been determined [7]. It was found that this compound crystallizes in the orthorhombic space group $Pca2_1$, with $Z=4$.

As part of our investigations of rare earth(III) compounds and as a continuation of our work on tetramethylammonium rare earth double sulphates, in the present paper the results of the synthesis and thermal decomposition of double sulphates of the other members of the rare earths(III), with the general empirical formula $(CH_3)_4NLn(SO_4)_2 \cdot 2H_2O$ (*Ln*=Ho–Lu and Y), are reported. A survey of the literature revealed no data on these compounds.

The X-ray powder diffraction patterns used only for the identification of the products are not presented here. The photos are to be found in the Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Slovenia.

## Experimental

### *Materials*

The rare earth oxides were used as starting compounds; they were treated as described in [9] to prepare concentrated solutions of rare earth sulphates. The concentrations of the rare earths in the solutions were determined gravimetrically after precipitation of the rare earths as oxalates and ignition to the oxides.

A solution of tetramethylammonium sulphate with a concentration of about 0.6 mol/dm$^3$ was prepared by neutralization, with constant cooling, of a 25%(mass) aqueous solution of tetramethylamine (BDH analytical reagent) with dilute sulphuric acid.

### *Synthesis of double salts*

When an aqueous mixture of a rare earth(III) sulphate and tetramethylammonium sulphate, in a molar ratio greater than 1:4, up to 1:12, was evaporated at ambient temperature, with subsequent treatment of the concentrated reaction mixture with ethanol, the double sulphate of the rare earths(III) with tetramethylammonium was obtained. The crystalline products were filtered off, washed with ethanol and dried in air. The products were identified as new compounds via their X-ray powder diffraction patterns and further studied by TG, DTG and DTA.

### *Thermal analysis*

The thermoanalytical curves were obtained on a Mettler Thermoanalyser TA 1 in dynamic dry air: flow rate 5 l/h; Pt/Pt-Rh thermocouples; Pt crucibles; sample mass approximately 100 mg; heating rate 6 deg·min$^{-1}$; reference for DTA determinations $\alpha$-$Al_2O_3$, in the temperature range from 20 to 700°C.

X-ray powder diffraction patterns were obtained with a Guinier de Wolff camera with $CuK_\alpha$ radiation.

The rare earth and sulphate contents were determined by gravimetry, as rare earth oxide and barium sulphate.

## Results and discussion

From the X-ray powder diffraction patterns of the compounds obtained, it was concluded that they are isostructural. It was also found that their crystal structure is different from the crystal structures of the two groups of tetramethylammonium rare earth double sulphate trihydrates recently presented [6]. On the basis of their isostructurality, the quantitative analyses of the rare earth and sulphate, and the determination of water from the TG curves the general empirical formula $(CH_3)_4NLn(SO_4)_2{\cdot}2H_2O$ (*Ln*=Ho–Lu and Y) was determined. These are not trihydrates, as is the case with the double sulphates of lighter lan-

**Table 1** TG data for $RLn(SO_4)_2{\cdot}2H_2O$ in the temperature interval from 20 to 700°

| Ln (Mr) | 1. stage (% $H_2O$) | 2. stage (% $R_2SO_4$) | 3. stage (% $SO_3$) | residue [% $Ln_2(SO_4)_3$] |
|---|---|---|---|---|
| Ho(467.22) | 8.21(7.71) | 22.97(26.15) | 12.28( 8.56) | 56.52(66.14) |
| Er(469.55) | 7.90(7.67) | 22.96(26.01) | 14.54( 8.52) | 54.60(66.31) |
| Tm(471.22) | 7.66(7.64) | 22.53(25.92) | 7.85( 8.49) | 61.50(66.43) |
| Yb(475.33) | 7.60(7.58) | 21.23(25.72) | 5.16( 8.42) | 66.34(66.70) |
| Lu(477.66) | 7.00(7.55) | 21.38(25.60) | 16.71( 8.48) | 54.91(66.85) |
| Y (392.20) | 9.10(9.18) | 27.12(31.16) | 12.43(10.20) | 51.35(59.66) |

* Found values in % for: Ho 34.45(35.30) and $SO_4^{2-}$ 40.23 (41.12); Y 22.84 (22.92) and $SO_4^{2-}$ 48.45(48.99)

Notes: The calculates values are given in brackets. *R*=$(CH_3)_4N$

thanides with the same monovalent cation [6]. The results of the analyses are given in Table 1.

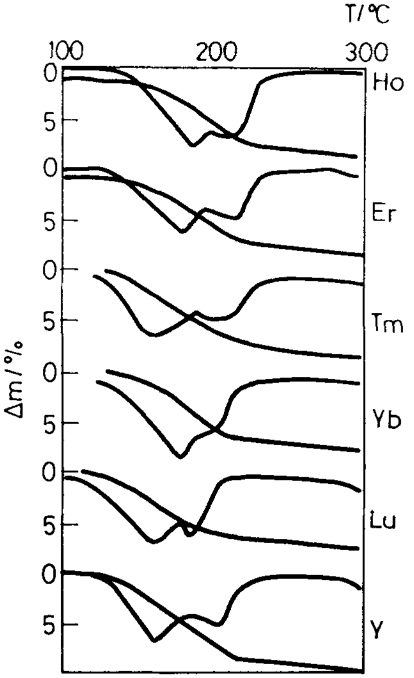

**Fig. 1** TG and DTG curves of the dehydration $(CH_3)_4NLn(SO_4)_2 \cdot 2H_2O$

The TG, DTG and DTA curves of the dehydration are presented in Fig. 1. The TG, DTG and DTA curves relating to thermal decomposition in the range from ambient temperature to 700°C are presented in Fig. 2. The thermal decomposition of each compound occurs in three well-differentiated stages. The first stage is related to the dehydration, and the second and third stages are due to the decomposition of the anhydrous double salt. Dehydration commences at temperatures greater than 100°C, takes place in two steps and ends at about 240°C. This means that evolution of the crystal water takes place at different rates (two peaks in the DTG curves; see also Table 2). The temperatures of the DTG maxima reveal that the stability of the crystallohydrates generally decreases from Ho to Lu (the Yb compound is an exception). The decomposition of the anhydrous double salts in the second and third stages is very complex and is related to several thermal events.

The second stage begins at about 300°C and ends at about 500°C. In this stage, the anhydrous double sulphate liberates tetramethylammonium sulphate and this stage corresponds to the thermal decomposition of free tetramethyl ammonium sulphate [6]. This also decomposes in air atmosphere (it begins at

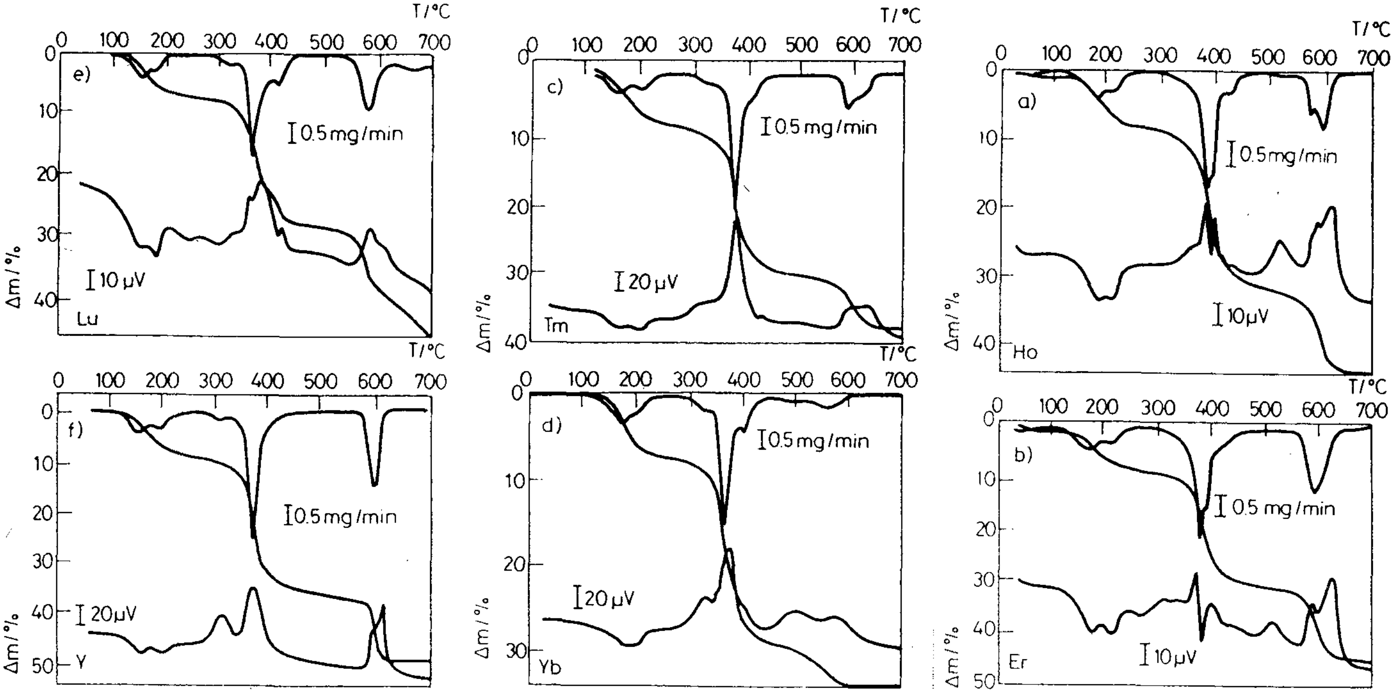

Fig. 2 TG, DTG and DTA curves of the thermal decomposition of $(CH_3)_4NLn(SO_4)_2.2H_2O$

**Table 2** Temperature relating to the DTG maxima by thermal decomposition of $(CH_3)_4NLn(SO_4)_2 \cdot 2H_2O$

| *Ln* | | | |
|---|---|---|---|
| Ho | 188, 215 | 390 | 583, 602 |
| Er | 180, 210 | 377 | 600 |
| Tm | 160, 200 | 374 | 587 |
| Yb | 177, 325 | 363 | 560 |
| Lu | 160, 184 | 330, 367, 418 | 587, 670 |
| Y | 162, 204 | 314, 371 | 598 |

about 250°C), with endothermic and exothermic effects, but in the case of this series of double sulphates, this process occurs at a higher temperature. Hence, tetramethylammonium sulphate is stabilized in these double salts. The residue mass (Table 1) is less than that calculated for $Ln_2(SO_4)_3$ (*Ln* = Ho, Er, Tm, Lu or Y), and is indicative of further decomposition of $Ln_2(SO_4)_3$ to $Ln_2O(SO_4)_2$ (or $Lu_2O_2SO_4$) in the third stage. This stage begins at a temperature higher than 530°C, the highest value being observed for the Y compound.

If these results are compared with those recently presented for the tetramethylammonium double sulphate trihydrates of the lighter rare earths [6], it can be concluded that the dehydration takes place by a different mechanism, but the thermal decomposition in the second stage proceeds in a similar way. At 500°C, the residual mass for all those double sulphates of rare earths with tetramethylammonium [6] and those studied here is greater than that calculated for the corresponding rare earth(III) sulphate. It is possible that part of the carbon liberated from the thermal decomposition of tetramethylammonium is included in the residue (at 500°C). The strong exotherm at about 600°C (Fig. 2, DTA curves) confirmed the possibility of the reaction between carbon and $Ln_2(SO_4)_3$, as described earlier [4] for double sulphates of rare earths with trimethylammonium. The fact that the temperature of the thermal decomposition of $Ln_2(SO_4)_3$ from the presented double sulphates is lower than 800°C, as described for pure $Ln_2(SO_4)_3$ [10, 11], is in agreement with what was found for the thermal decomposition of trimethyl rare earth(III) sulphate trihydrates [4]. The decreasing temperature of the thermal decomposition can be attributed to the reduction of the rare earth(III) sulphate by the carbon produced in the thermal decomposition of alkylammonium sulphate.

The behaviour of the Yb salt is anomalous in that the second and third stages are very close and ytterbium(III) sulphate is obtained as final product.

Hence, the thermal decompositions of the tetramethylammonium rare earth(III) sulphate dihydrates can generally be represented by the following equations:

1st stage: $(CH_3)_4NLn(SO_4)_2{\cdot}2H_2O \rightarrow 2H_2O+(CH_3)_4NLn(SO_4)_2$

2nd stage: $2(CH_3)_4NLn(SO_4)_2 \rightarrow [(CH_3)_4N]_2SO_4+Ln_2(SO_4)_3$

3rd stage: $Ln_2(SO_4)_3+C \rightarrow Ln_2O(SO_4)_2+CO+SO_2$

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**Zusammenfassung** — Werden Reaktionsgemische von Seltenerden(III)-sulfaten und Tetramethylammoniumsulfat in molaren Verhältnissen von 1:4 bis 1:12 bei Umgebungstemperatur eingedampft und die konzentrierten Reaktionsgemische mit Ethanol behandelt, erhält man als Reaktionsprodukte Doppelsulfate der allgemeinen empirischen Formel $(CH_3)_4NLn(SO_4)_2{\cdot}2H_2O$ ($Ln$=Ho-Lu und Y). Die kristallinen Produkte wurden mittels quantitativer Analyse, Debye-Scherrer-Aufnahmen sowie TG-, DTG- und DTA-Analyse identifiziert und besitzen die gleiche Struktur. Ihre thermische Zersetzung verläuft in drei Schritten. Der Temperaturbereich der Dehydratation nimmt von Ho bis Lu Hauptsächlich ab. Mit der thermischen Zersetzung im zweiten und dritten Schritt gehen zahlreiche thermische Ereignisse einher. Als Endprodukt wird $Ln_2O(SO_4)_2$ erhalten.