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DOUBLE DIMETHYLAMMONIUM SULPHATES OF Tb, Dy, Ho, Er, Tm, Yb, Lu AND Y

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Double sulphates of rare earths with dimethylammonium, with empirical formula $(CH_3)_2NH_2Ln(SO_4)_2\cdot 4H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), were studied by means of thermogravimetry, derivative thermogravimetry and differential thermal analysis from 20 to 700°. Quantitative gravimetric analysis was used for the determination of rare earths and sulphate. The mechanism of thermal decomposition is also suggested.

There are many data about the salts and double salts of rare earths [1–7]. The thermal decompositions of some double sulphates of rare earths with monovalent cations were studied by Zajceva et al. [8], Ishakova et al. [9] and Bukovec et al. [4].

The crystal structure of $(CH_3)_2NH_2Ln(SO_4)_2\cdot 4H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb and Y) was recently solved. The compounds proved to be isomorphous, all of them crystallizing in the same space group Pnma (No. 62) with 4 formula units in the crystal unit cell [10].

In this paper we give the results of chemical and thermal analysis for $(CH_3)_2NH_2Ln(SO_4)_2\cdot 4H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y).

Experimental

Materials

The rare earth oxides were used as starting compounds; they were treated as described in [11] 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 dimethylammonium sulphate with a concentration of about 0.5 mol/dm^3 was prepared by neutralization of a 25% solution of dimethylamine with dilute H_2SO_4.

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Procedure. By isothermal evaporation at room temperature and by treating with ethanol concentrated aqueous mixed solutions of $Ln_2(SO_4)_3$ and $[(CH_3)_2NH_2]_2SO_4$ in molar ratios from 1 : 4 up to 1 : 10, double sulphate tetrahydrates with empirical formula $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) have been obtained. Besides these double sulphates, monohydrates (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) have also been isolated, and at a molar ratio higher than 1 : 10 another kind of double sulphate with empirical formula $[(CH_3)_2NH_2]_3Ln(SO_4)_3 \cdot 3H_2O$ (Ln = Nd, Sm, Eu, Gd and Tb) resulted.

The obtained double sulphates were studied by quantitative analysis, X-ray diffraction and the methods of differential thermoanalysis, thermogravimetry and derivative thermogravimetry.

Methods

The thermoanalytical curves were obtained with a Mettler thermoanalyser in a flow of dry air or argon.

Experimental conditions: sample mass 100 mg; reference substance for DTA determination α-Al_2O_3; TG macro sample holder with Pt crucibles; heating rate 6 deg/min; temperature range from 20° to 700°.

Table 1 The results of thermal and chemical analysis of the double sulphates $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$

Ln (Mr)	Mol. rat.	% H_2O	% $Ln_2(SO_4)_3$	% $(CH_3)_2NH_2$ $_2SO_4$	% Ln^{3+}	% SO_4^{2-}
Tb (469.19)	1 : 10	15.36	64.58	20.06		
		15.20	64.97	19.83		
Dy (472.77)	1 : 6	15.24	64.64	19.91		
		15.40	63.45	21.15		
Ho (475.20)	1 : 4	15.16	65.03	19.81		
		15.08	63.47	21.45		
Er (477.53)	1 : 6	15.09	65.52	19.71	35.03	40.23
		15.17	65.47	19.36	34.46	39.92
Tm (479.20)	1 : 6	15.04	65.32	19.64		
		15.24	65.23	19.53		
Yb (483.31)	1 : 10	14.91	65.62	19.47		
		14.89	65.43	19.68		
Lu (485.24)	1 : 6	14.85	65.75	19.40		
		14.90	65.62	19.48		
Y (399.16)	1 : 10	18.05	58.37	23.58		
		18.20	57.90	23.90		

The contents of the rare earths in the double sulphates were determined gravimetrically as mentioned above. The contents of sulphate were also determined gravimetrically, as $BaSO_4$. The results are given in Table 1.

Results and discussion

TG, DTG and DTA curves are shown in Figs 1–4. The experimental and calculated weight losses, together with the results of quantitative chemical analysis, are given in Table 1.

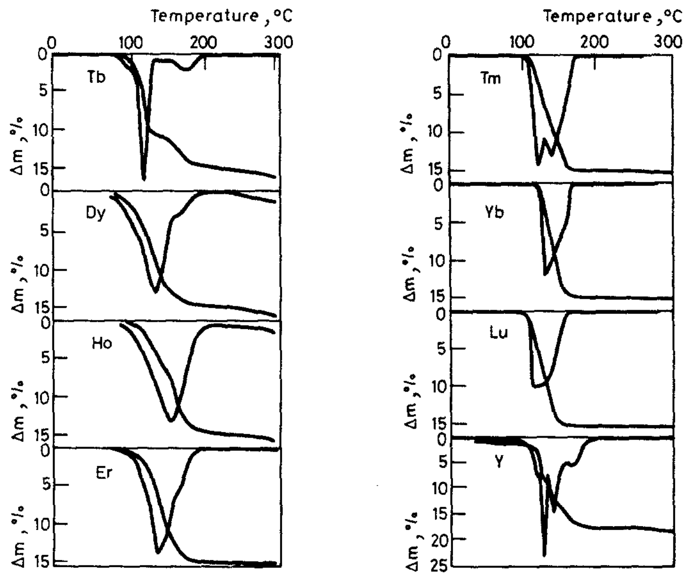

Fig. 1 DTG and TG curves of dehydration of $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$

The TG and DTG curves are similar for all the compounds, indicating two stages of thermal decomposition. In the first stage, dehydration occurs with an endothermic effect in one step (DTA curves). Exceptions are the double sulphates of Tb and Tm, which dehydrate in two close steps, and that of Y, which dehydrates in three steps. For the compounds from Tb to Ho an increase is observed in the temperature of the DTG maximum, but from Ho to Yb there is a steady decrease in this temperature with increasing atomic number of the rare earths (Fig. 1).

The dehydration of the double sulphates in one step or in two very close steps indicates that the water molecules are equivalent, as can also be seen from the structural data [10] for these compounds. The temperature difference between the

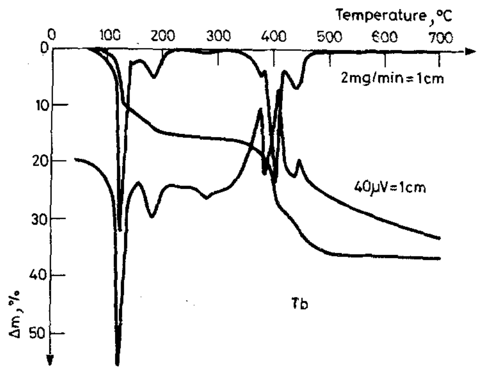

Fig. 2 DTG, TG and DTA curves of $(CH_3)_2NH_2Tb(SO_4)_2 \cdot 4H_2O$

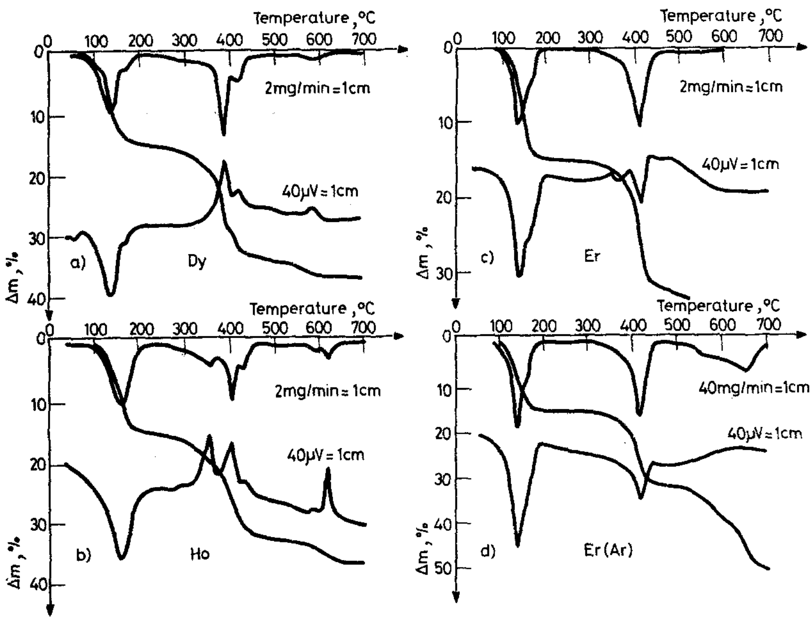

Fig. 3 DTG, TG and DTA curves of $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$

two stages of thermal decomposition is fairly large (about 200°) and it is possible to obtain the anhydrous double sulphates by isothermal dehydration.

The second stage of thermal decomposition, in the temperature interval from 357° to 448°, takes place in three steps for the double sulphates of Tb, Ho, Tm and Lu, and in two steps for those of Dy, Yb, Er and Y, as can be seen from the DTG curves (Figs 2–4). The DTA peaks show that in this stage the thermal decompositions of the anhydrous double sulphates are very complex and proceed

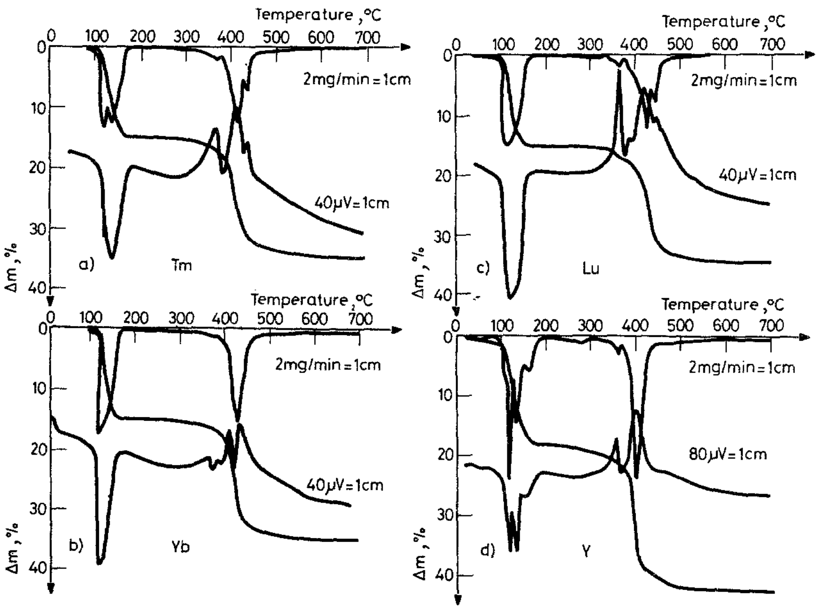

Fig. 4 DTG, TG and DTA curves of $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$

via intermediates which were almost impossible to isolate because the temperature differences between the steps were very small.

The thermal decomposition of $(CH_3)_2NH_2Er(SO_4)_2 \cdot 4H_2O$ in an inert atmosphere of argon (Fig. 3d) is similar to that in air in the first stage, but no exothermic effect appears in the second stage (see DTa curves in Figs 3c and 3d). This means that in the second stage of decomposition oxidation of the CH_3 groups takes place in the presence of oxygen.

We presume that the DTG peaks (Figs 3b and 3a) at 588° for Ho and at 585° for Dy are the result of the later oxidation of carbon. From X-ray powder data on the final products at 700°, it was concluded that rare earth sulphates are obtained. This is in agreement with the results of thermal decomposition of rare earth sulphates [4, 12, 13], which decompose at temperatures higher than 700°.

In general, the thermal decomposition can be written as:

$$(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O \xrightarrow[-4H_2O]{\text{stage I}} (CH_3)_2NH_2Ln(SO_4)_2$$

$$2\,(CH_3)_2NH_2Ln(SO_4)_2 \xrightarrow[-[(CH_3)_2NH_2]SO_4]{\text{stage II}} Ln_2(SO_4)_3$$

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Zusammenfassung — Doppelsulfate der seltenen Erden mit Dimethylammoniumionen der empirischen Formel $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu und Y) wurden mittels TG, DTG und DTA im Temperaturbereich von 20–700° untersucht. Die Seltenen Erden und Sulfat wurden gravimetrisch bestimmt. Ein Mechanismus der thermischen Zersetzung wird vorgeschlagen.

Резюме — Методом ТГ, ДТГ и ДТА изучено в температурном интервале 20–700° термическое поведение двойных солей диметиламмония и сульфатов редкоземельных элементов эмпирической формулы $(CH_3)_2NH_2Ln(SO_4)_2 \cdot 4H_2O$, где Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu и Y. Для определения редкоземельных элементов и сульфатных групп был использован количественный гравиметрический анализ. Предложен также механизм термического разложения солей.