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Synthesis, characterization and thermal decomposition of double sulfates of trivalent Al and Fe with di- or triethanolammonium monovalent cations

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Abstract

By evaporation of an aqueous mixture of M(III) sulfate and diethanolammonium sulfate or triethanolammonium sulfate in the presence of sulfuric acid, double sulfates of Al(III) and Fe(III) were obtained. The stoichiometries of the compounds obtained were determined by means of elemental and TG analyses. It was found that they have the following general formulae: $Al(HOCH_2CH_2)_2NH_2(SO_4)_2{\cdot}6H_2O$; $Al(HOCH_2CH_2)_3NH(SO_4)_2{\cdot}6H_2O$; $Fe(HOCH_2CH_2)_2NH_2(SO_4)_2{\cdot}4H_2O$; $Fe(HOCH_2CH_2)_3NH(SO_4)_2{\cdot}6H_2O$.

From the X-ray powder diffraction patterns, it was concluded that the investigated compounds have different crystal structures. It was also established, from the TG curves, that they lose water at low temperature and also that the anhydrous double salts decompose at low temperature (at about 523 K).

Keywords: Double sulfates of Al(III) and Fe(III) with di- or triethanolammonium; Synthesis; Thermal studies

1. Introduction

The double sulfates of Al(III) and Fe(III) with monovalent metal cations and ammonium which crystallize as dodecahydrates, are well investigated and are known as a group of alums. The double sulfates with monomethylammonium are also alums

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[1,2]. There are also some data on the synthesis and thermal decomposition of compounds of Al(III), Cr(III) and Fe(III) with various alkylammonium cations, such as methylammonium and diethylammonium [3–5], with a stoichiometry different from that of the alums. The crystal structures of the isomorphous double sulfates of Al and Cr with dimethylammonium have been presented recently [6].

Continuing our work on the double sulfates of M(III) or M(II) with organic cations, we present in this paper results on the preparation and characterization of double sulfates of Al(III) and Fe(III) with diethanolammonium and triethanolammonium cations, on which we have not found any data. The thermal behavior of these compounds in static air, in the temperature range from 293 up to 1273 K has also been investigated.

2. Experimental

2.1. Chemicals

Analytical grade aluminum was used for the preparation of aluminum sulfate solution ($c = 0.5$ mol dm^{-1}) by dissolving pure aluminum foil in diluted sulfuric acid. $Fe_2(SO_4)_3 \cdot 9H_2O$, puriss (Alkaloid, Skopje), diethanolamine pract. (Fluka AG), and triethanolamine, for synthesis (Merck) were employed.

2.2. Synthesis of double sulfates

Double sulfates of M(III) with diethanolammonium and triethanolammonium cations were obtained as products by evaporation at ambient temperature of a concentrated aqueous reaction mixture of M(III) sulfate (0.008 mol) and di- and triethanolammonium sulfate in a molar ratio higher than 1:4, with addition of sulfuric acid (0.008 mol). The concentrated solutions of diethanolammonium sulfate and triethanolammonium sulfate were obtained by neutralization of diethanolamine or triethanolamine with diluted sulfuric acid, step-wise to pH 4, and permanent cooling in an ice-water bath. The obtained crystalline products were separated by filtration, washed with ethanol and dried in a desiccator. For identification of the products obtained, X-ray powder diffraction patterns were made. For determination of their stoichiometry, elemental analysis, and TG, DTG and DTA were performed. The results of the elemental analysis are given in Table 1.

2.3. Analytical section

Elemental analyses for carbon and hydrogen were done using Liebig's method and a carbon–hydrogen analyzer (Coleman Model 33); analysis for nitrogen was by the Dumas method.

The X-ray powder diffraction patterns were recorded on a Philips PW 1050 vertical goniometer with a proportional counter using graphite-monochromatized CuKα radiation. The patterns can be found at the Institute of Chemistry of Skopje.

Table 1
Results of elemental analysis

Compound	%, found/calculated		
	C	H	N
$Al(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 6H_2O$	11.50	5.92	3.10
	11.09	5.58	3.23
$Al(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$	14.50	6.67	2.36
	15.09	5.90	2.93
$Fe(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 4H_2O$	11.83	5.30	3.95
	11.27	4.73	3.29
$Fe(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$	13.90	4.76	2.10
	14.23	5.57	2.77

2.4. *Thermal studies*

TG, DTG and DTA curves for the Al compounds were performed using a Derivatograph Q (Hungary) in static air atmosphere at a heating rate of 10 K min^{-1} over the range 293–1273 K, using a 100 mg sample in Pt crucibles. Sensitivity: TG, 100 mg; DTG, 1 mV; DTA, 0.5 mV. The reference substance was pure alumina.

TG curves for the Fe compounds were performed using a Cahn RG Electrobalance in air atmosphere at a heating rate of 5 K min^{-1} over the range 293–1123 K and using 10–12 mg of sample in a quartz crucible. The DTA was performed using a Netzsch differential thermal analyzer. The DTA curves were obtained in static air atmosphere with sample masses of 70–100 mg at a heating rate of 5 K min^{-1} from ambient temperature to about 1123 K.

3. Results and discussion

From the X-powder diffraction patterns of the products, it was established that they have different crystal structures. Their patterns are also different from those of the starting compounds. Because it was not possible to obtain a solid product by evaporation of an aqueous solution of ethanolammonium sulfates, we assumed that they are not included as crystals in the obtained products. From the results of the elemental analysis (Table 1) and the TG curve, it was established that double sulfate crystallohydrates of M(III) with ethanolammonium cations were obtained:

$Al(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 6H_2O$

$Al(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$

$Fe(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 4H_2O$

$Fe(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$

The above aluminum double sulfates are also hexahydrates, as we have established for other aluminum(III) double sulfates with dimethylammonium, trimethylammonium and diethylammonium [3-6], but the number of water molecules in both Fe(III) compounds is different and in general varies in alkylammonium double sulfates. Comparing the X-ray powder diffraction patterns of the above compounds with the ones recently presented for M(III) (Al,Fe) double sulfates with ethanolammonium sulfate [7], it is found that they are different. Because it is known that alums of Al(III) and Fe(III) are isostructural whereas double sulfates of the same trivalent cations with dimethylammonium, trimethylammonium, and ethanolammonium [3, 5-7] are not, it could be supposed that the type and size of a monovalent cation has a great influence on the crystal structure of the double sulfates of M(III), as established for double sulfates of M(II) with different monovalent cations [8]. We also tried to obtain a double sulfate of Cr(III) with ethanolammonium cations and of M(II) (Mn, Fe, Co, Ni, Cu, Zn and Cd) with di- and triethanolammonium cations (synthesis of double sulfates with ethanolammonium was attempted recently [9] under the conditions described in the Experimental part, but we were unsuccessful).

4. Thermal decomposition

Thermal decomposition of both Al(III) double sulfates takes place in a similar manner (Figs. 1 and 2) to that of double sulfates of Al(III) and Fe(III) with ethanolammonium, as recently presented [7]. It is very difficult to resolve the two steps of the thermal decomposition, but from the TG and DTG peaks we tried to separate the dehydration process from the decomposition of the anhydrous double salts. Dehydration occurs in two steps (see DTG curves) which indicates that evolution of water takes place at different temperatures and at different rates. The second step, thermal decomposition of anhydrous double salt, is very complex. Many thermal effects on the DTA curves, endothermal and exothermal, lead us to the conclusion that this process is not only a dissociation but also an oxidation-reduction process. The fact that this process mainly ends at temperatures of about 873 K, which is much lower than the corresponding process of pure aluminum sulfate [10], suggests that the presence of carbon liberated from organic monovalent cation decreases the temperature of $Al_2(SO_4)_3$ dissociation. This is in agreement with the results of the investigation of the thermal decomposition of aluminum potassium sulfate in the presence of carbon and water vapor [11]. Thermal decomposition of the above compounds could be presented as in the following equations

1st step

$$Al(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 6H_2O \xrightarrow[-6H_2O]{313-493K} Al(HOCH_2CH_2)_2NH_2(SO_4)_2$$

Mass loss, 25.0%; calculated value, 25.5%

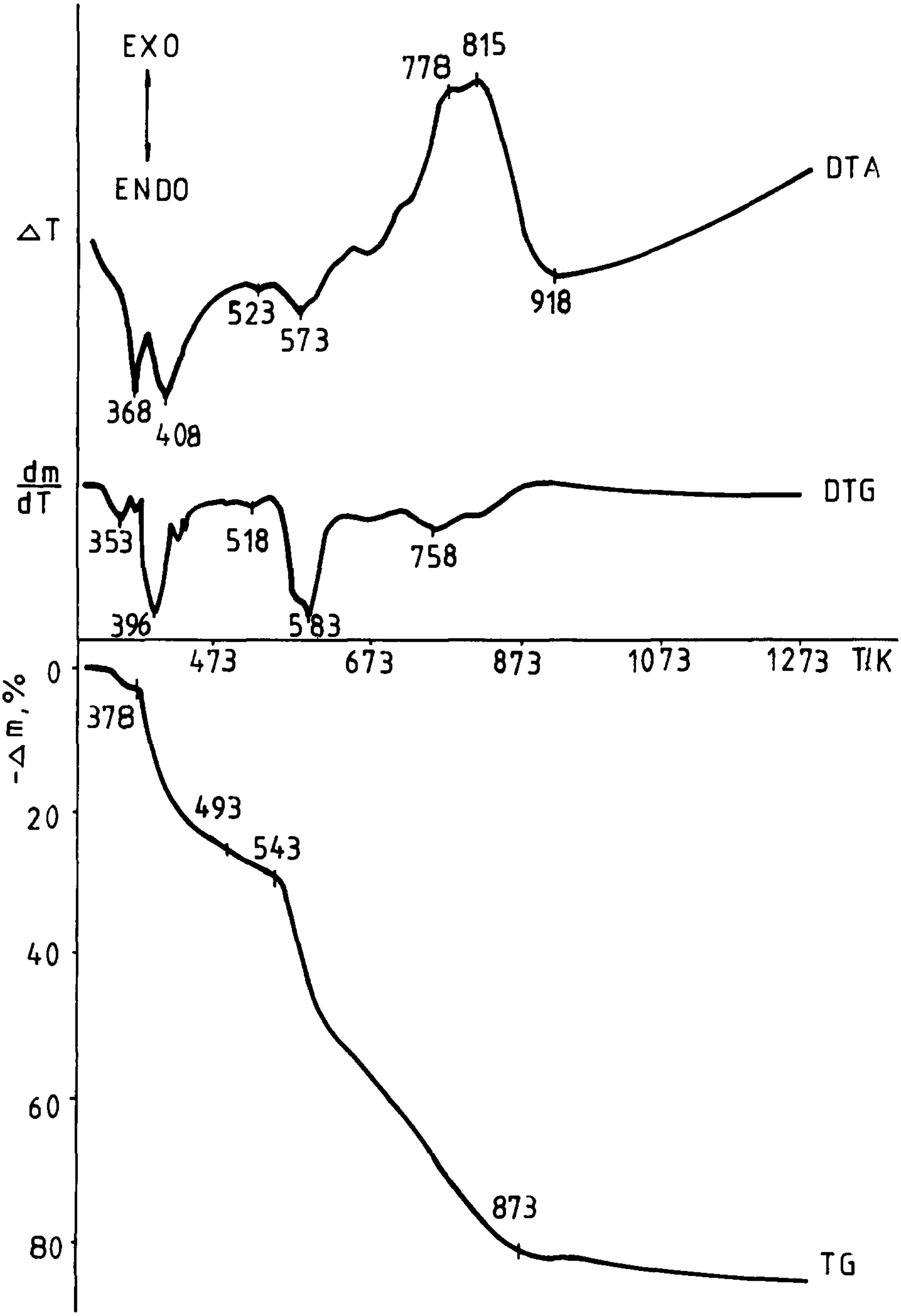

Fig. 1. TG, DTG and DTA curves of the thermal decomposition of $Al(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 6H_2O$.

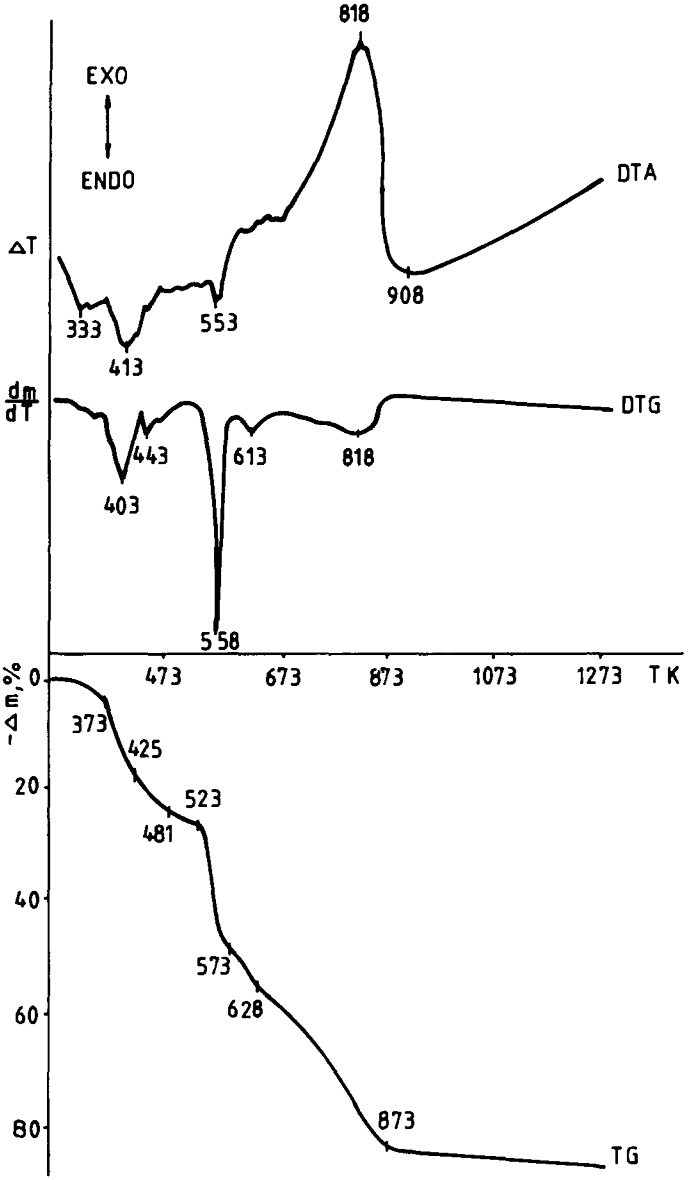

Fig. 2. TG, DTG and DTA curves of the thermal decomposition of $Al(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$.

2nd step

$$2Al(HOCH_2CH_2)_2NH_2(SO_4)_2 \xrightarrow[-[(HOCH_2CH_2)_2NH_2]_2SO_4,\ -3SO_3]{493-1273\,K} Al_2O_3$$

Mass loss, 63.5%; calculated value, 62.74%.

The obtained mass of the residue is 11.5%; the calculated value for aluminum oxide is 11.76%.

For the second Al compound

1st step

$$\mathrm{Al(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O \xrightarrow[-6H_2O]{313-481\,K} Al(HOCH_2CH_2)_3NH(SO_4)_2}$$

Mass loss, 24.0%; calculated value, 22.64%.

2nd step

$$\mathrm{2Al(HOCH_2CH_2)_3NH(SO_4)_2 \xrightarrow[-[(HOCH_2CH_2)_2NH_2]_2SO_4,\ -3SO_3]{493-1273\,K} Al_2O_3}$$

Mass loss, 64.0%; calculated value, 66.68%.

The obtained mass of the residue is 10.0%; the calculated value for aluminum oxide is 10.68%.

The thermal decompositions of iron(III) diethanolammonium sulfate tetrahydrate and iron(III) triethanolammonium sulfate hexahydrate take place in a similar manner (Figs. 3 and 4), which is different from that for the aluminum(III) compounds. Three decomposition steps could be distinguished, more clearly than in the TG curves of Al compounds. The first step is connected with the step-wise evolution of water. In the second step, decomposition of the anhydrous double salt takes place. This is connected with endothermal and exothermal effects. The last step could be attributed to the formation of intermediary products, as in the thermal decomposition of dimethylammonium iron(III) sulfate, presented recently [4]. In this step, $\mathrm{Fe_2O(SO_4)_2}$ is obtained. However, it is known that in the thermal decomposition of ammonium iron(III) sulfate [10], Fe(III) sulfate can exist up to 1023 K after loosing ammonium sulfate at about 708 K. But in the case of the thermal decomposition of ethanolammonium iron(III) sulfate dihydrate recently presented [7], in this temperature region iron(III) oxysulfate is also obtained. This could be attributed to the static conditions in which the presence of oxygen is limited. The carbon which is obtained by combustion of the organic cation could reduce the sulfate group to $\mathrm{SO_2}$, as proposed earlier for other alkylammonium double sulfates [4]. The formation of oxysulfate is related to the exothermic peaks. In the third step, the thermal decomposition of iron(III) oxysulfate to iron(III) oxide takes place. The X-ray powder diffraction patterns of the residues confirm that iron(III) oxide is obtained (File No. 13-534 [12]). The above processes can be expressed in the following equations

1st step

$$\mathrm{Fe(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 4H_2O \xrightarrow[-4H_2O]{323-523\,K} Fe(HOCH_2CH_2)_2NH_2(SO_4)_2}$$

Mass loss, 16.8%; calculated value, 16.90%.

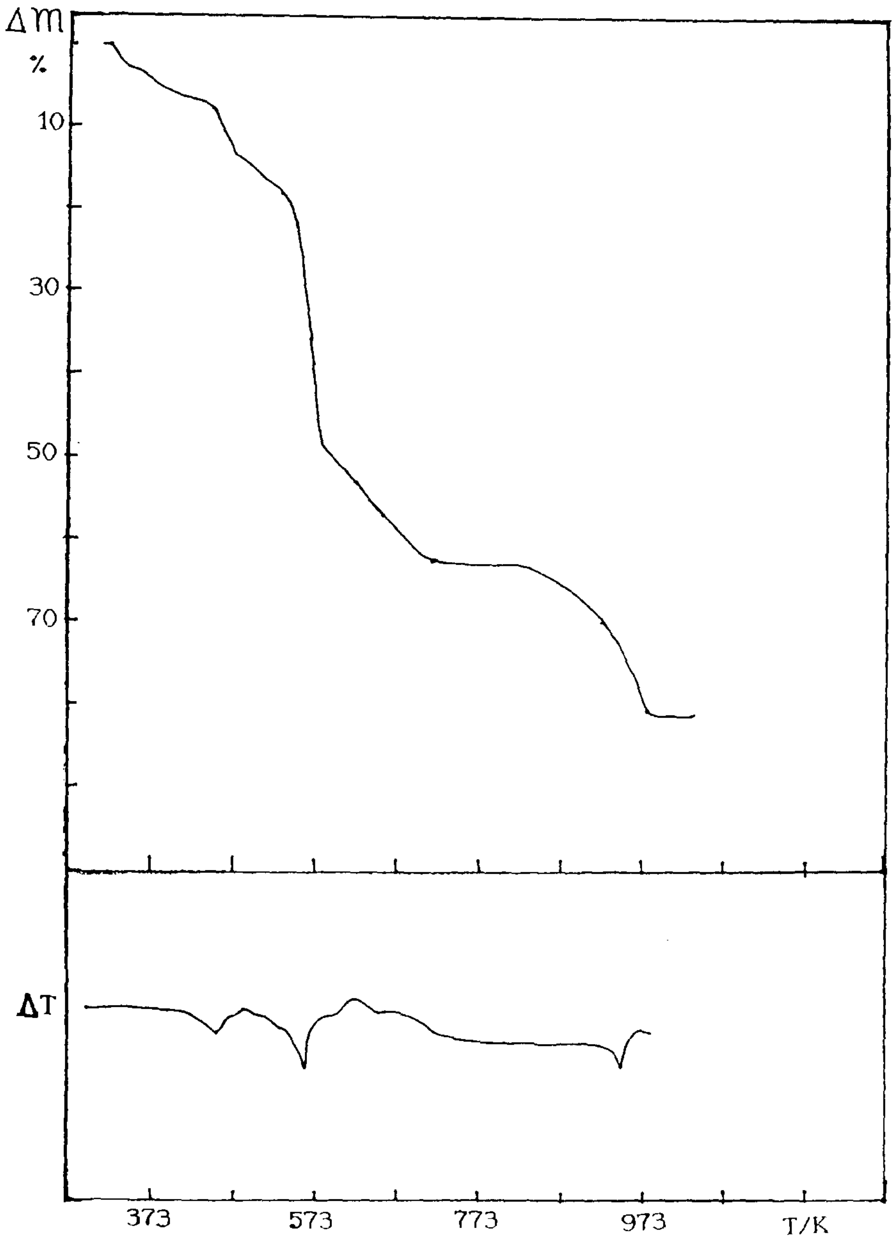

Fig. 3. TG and DTA curves of the thermal decomposition of $Fe(HOCH_2CH_2)_2NH_2(SO_4)_2 \cdot 4H_2O$.

2nd step

$$2Fe(HOCH_2CH_2)_2NH_2(SO_4)_2 \xrightarrow[-[(HOCH_2CH_2)_2NH_2]_2SO_4]{523-623\,K} Fe_2(SO_4)_3$$

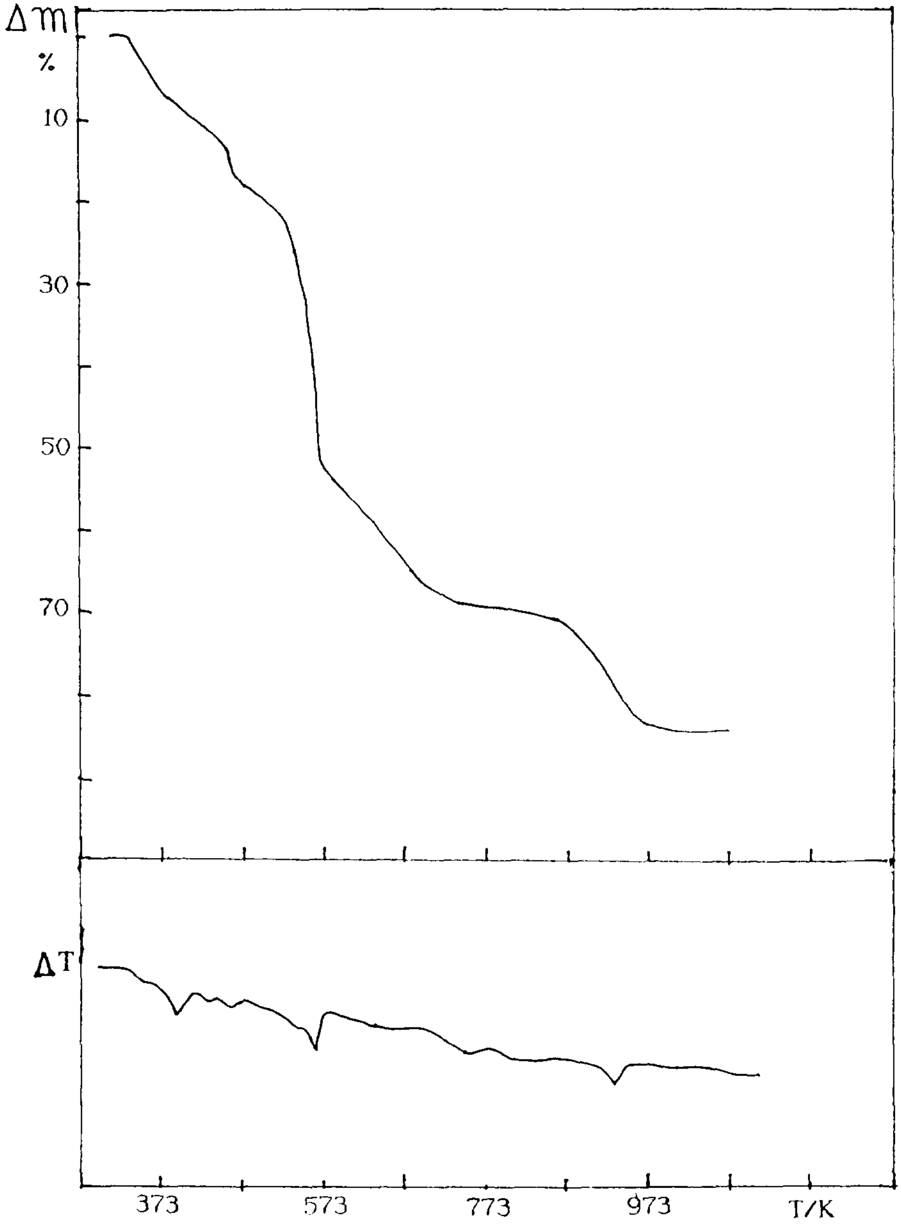

Fig. 4. TG and DTA curves of the thermal decomposition of $Fe(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O$.

Mass loss, 36.20%; calculated value, 36.17%.

$$Fe_2(SO_4)_3 \xrightarrow[-SO_3]{623-723\,K} Fe_2O(SO_4)_2$$

Mass loss, 9.0%; calculated value, 9.06%.

3rd step

$$Fe_2O(SO_4)_2 \xrightarrow[-2SO_3]{723-1043K} Fe_2O_3$$

Mass loss, 18.46%; calculated value, 18.11%.

The mass of the residue is 19.46%; the calculated value for iron(III) oxide is 19.74%.

For the second Fe(III) compound

1st step

$$Fe(HOCH_2CH_2)_3NH(SO_4)_2 \cdot 6H_2O \xrightarrow[-6H_2O]{333-513K} Fe(HOCH_2CH_2)_3NH(SO_4)_2$$

Mass loss, 21.0%; calculated value, 21.36%.

2nd step

$$2Fe(HOCH_2CH_2)_3NH(SO_4)_2 \xrightarrow[-[(HOCH_2CH_2)_2NH_2]_2SO_4,\ -SO_3]{513-771K} Fe_2O(SO_4)_2$$

Mass loss, 47.91%; calculated value, 47.06%

3rd step

$$Fe_2O(SO_4)_2 \xrightarrow[-2SO_3]{771-1079K} Fe_2O_3$$

Mass loss, 15.22%; calculated value, 15.81%.

The mass of the residue is 15.87%; the calculated value is 15.77%.

5. Conclusions

1. Double sulfates crystallohydrates of Al(III) and Fe(III) with di- and triethanolammonium were obtained.
2. Under the same conditions, Cr(III) and M(II) sulfates did not yield solid products with di- or triethanolammonium sulfate.
3. The double sulfates of Al(III) and Fe(III) are not isostructural and have a different stoichiometry.
4. Their crystal structure is also different from that of double sulfates with other alkylammonium monovalent cations.
5. The anhydrous double sulfates decompose at low temperatures, beginning at about 523 K, with many thermal events.
6. As final products, M(III) oxides were obtained at 1273 K.

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