

VERA JORDANOVSKA

SYNTHESIS, IDENTIFICATION AND THERMAL BEHAVIOUR OF SOME DOUBLE SULPHATES OF Al(III) AND Cr(III) WITH ALKYLAMMONIUM MONOVALENT CATIONS

Abstract: By evaporation of an aqueous mixture of M(III) sulphate and alkyl ammonium sulphate in the presence of sulphuric acid, double sulphates were obtained. The stoichiometries of double sulphates were determined by means of elemental and thermal analysis as well as by determination of M(III) oxide by ignition of double sulphate at 900°. TG, DTG, DTA and DSC curves in dynamic conditions indicated a complicated decomposition, involving the formation of intermediate products. All double sulphates are hexahydrates, but the ratio between M(III) and alkyl ammonium varies. An assumption was made, that M(III) is surrounded with six molecules of water as by alums.

Introduction

Double sulphates of M(III) and monovalent alkali metals, Tl(I) and methylammonium are the subject of many investigations. In the group of double sulphates dodecahydrates, known as alums, belong double sulphates dodecahydrates of Al(III), Cr(III) and Fe(III). The crystal structure and dimorphism of alums [1-7] as well as some of their physical properties were also studied [2]. Thermal decomposition of Al-alums has also been investigated [8]. There are, also, a few data on double sulphates of M(III) with other alkylammonium monovalent cations. The results of thermal decomposition of isomorphous aluminium(III) and chromium(III) dimethylammonium sulphate hexahydrates are presented [9]. The synthesis and thermal decomposition of some double sulphates of iron(III) with some alkylammonium cations have been investigated [12] and a difference in thermal decomposition in air as opposed to an inert atmosphere has been found.

This paper presents the results of the synthesis, identification and thermal decomposition of double sulphates of Al(III) with diethyl-, trimethyl- and tetramethylammonium and of Cr(III) with diethylammonium. These inves-

tigations are a part of our work on the synthesis and characterisation of double sulphates of M(III) with non-classical ions such as monomethyl-, dimethyl-, diethyl-, trimethyl- and tetramethylammonium cations.

Experimental

Procedure and methods

Double sulphates of Al(III) and Cr(III) with methylammonium cations were obtained by evaporation of a concentrated aqueous mixture of M(III) sulphate and alkylammonium sulphate in molar ratio from 1:4 to 1:10 in the presence of sulphuric acid. The obtained crystalline product was filtered off, washed with ethanol and dried on air. For identification, X-ray powder diffraction patterns, elemental and thermal analyses were undertaken. X-ray powder diffraction patterns used only for identification are not presented.

Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves were obtained on the Mettler Thermoanalyser in a flow of dry air at a rate of 5 L/h, at a temperature interval from 20 to 600°, Pt/Pt-Rh thermocouple, Pt-crucibles (TD₁), a heating rate 6°/min, a reference substance for DTA determinations α -Al₂O₃. The mass of the sample was about 100 mg.

TG and DTA curves in an atmosphere of nitrogen were obtained on the Netzch Thermoanalyser MSTA 429 in a flow of dry nitrogen at a rate of 5L/h, Pt/Pt-Rh thermocouple, using quartz crucibles, a sample mass of about 30 mg, a heating rate of 2°/min, in a temperature interval from 20 to 500°. The reference substance for DTA determinations was α -AL₂O₃.

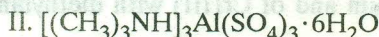
TG and DSC curves were obtained on the Mettler Thermoanalyser in a flow of dry air. Experimental conditions: TG macrosample holder with Pt-crucibles, heating rate of 4°/min, temperature range from 20 to 700°. A reference substance for DSC determinations was α -Al₂O₃.

Results and discussion

By reaction of aluminium(III) sulphate with trimethylammonium sulphate, depending on molar ratio, two different products are obtained:



in molar ratio from 1:4 to 1:6, and



in molar ratio higher than 1:8 e.g. as 2nd fraction of crystallisation in molar ratio 1:8. These empirical formulas were determined by elemental and thermal analysis. The results are given in Table 1.

Table 1

Results of elemental and thermal analysis of double sulphates of Al(III) and Cr(III) with alkylammonium cations

% of	Al-DEAM-S (401.24 g·mol ⁻¹) (m.r. 1 : 8)	Cr-DEAM-S (670.55 g·mol ⁻¹) (m.r. 1 : 8)	Al-TEMAM-S (401.24 g·mol ⁻¹) (m.r. 1 : 4)
C	12.59 (11.97)	21.05 (21.41)	12.35 (11.97)
H	6.03 (6.03)	6.88 (7.22)	6.00 (6.03)
N	3.64 (3.49)	6.75 (6.27)	3.64 (3.49)
M	6.63 (6.72)	—	6.33 (6.72)
M ₂ O ₃	12.53 (12.71)	—	11.96 (12.71)
H ₂ O	26.83 (26.94)	16.40 (16.12)	26.11; 27.06* (26.94)
R ₂ SO ₄	31.71 (30.44)	55.80 (54.65)	— (30.44)
M ₂ (SO ₄) ₃	— (42.62)	— (29.23)	— (42.62)
Other residue	16.02	18.50	20.74; 10.80*

	Al-TRMAM-S(II) (603.25 g·mol ⁻¹) (m.r. 1 : 8)	Al-TRMAM-S(I) (387.06 g·mol ⁻¹) (m.r. 1 : 6)
C	17.60 (17.02)	10.76 (9.85)
H	6.89 (7.02)	5.83 (5.91)
N	7.09 (6.97)	4.43 (3.74)
M	5.24 (4.47)	7.22 (6.95)
M ₂ O ₃	9.91 (8.45)	13.65 (13.17)
H ₂ O	—	26.03 (27.80)
R ₂ SO ₄	—	— (27.94)
M ₂ (SO ₄) ₃	—	— (44.16)
		15.59

Calculated values are given in brackets.

Al-DEAM-S = (C₂H₅)₂NH₂Al(SO₄)₂·6H₂O

Cr-DEAM-S = [(C₂H₅)₂NH₂]₃Cr(SO₄)₃·6H₂O

Al-TEMAM-S = (CH₃)₄NAl(SO₄)₂·6H₂O

Al-TRMAM-S(II) = [(CH₃)₃NH]₃Al(SO₄)₃·6H₂O

Al-TRMAM-S(I) = (CH₃)₃NHAl(SO₄)₂·6H₂O

R is alkylammonium cation.

* Obtained values in nitrogen

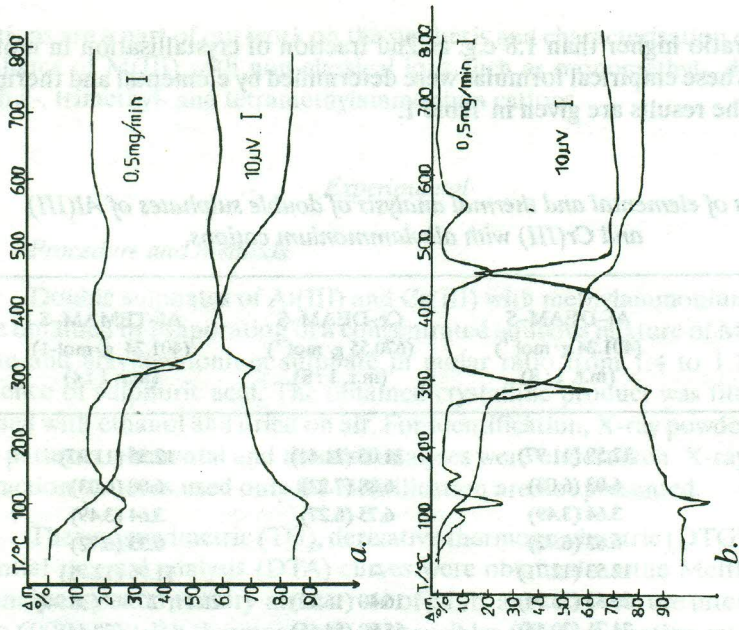


Fig. 2 - TG, DTG and DTA curves of thermal decomposition of
a) $(C_2H_3)_2NH_4Al(SO_4)_2 \cdot 6H_2O$ and b) $(C_2H_3)_2NH_4Cr(SO_4)_3 \cdot 6H_2O$

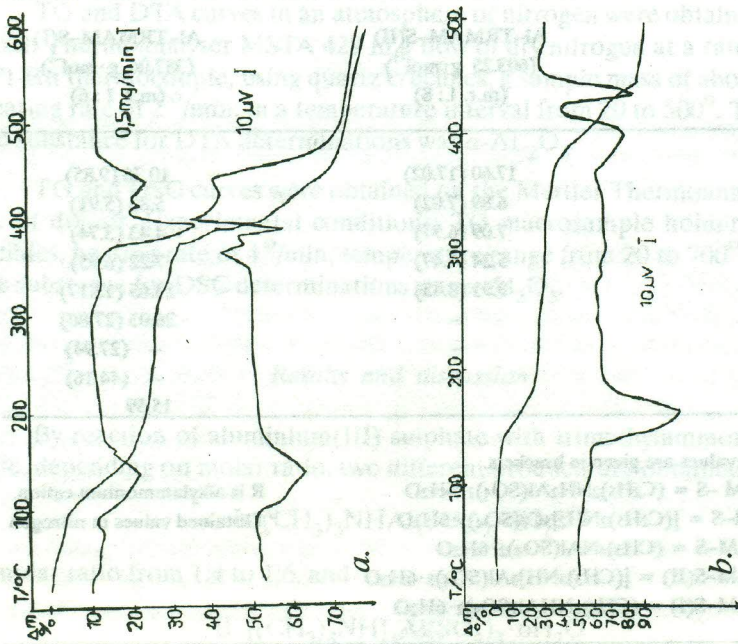


Fig. 1 - TG, DTG and DTA curves of thermal decomposition of
 $(CH_3)_4NAl(SO_4)_2 \cdot 6H_2O$ a) in air and b) in nitrogen

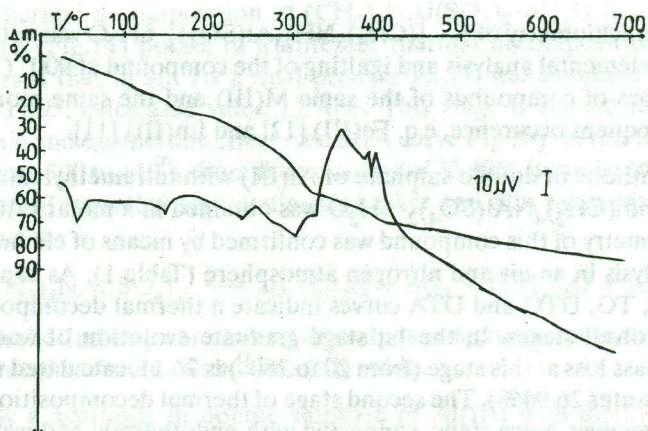
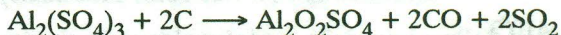


Fig. 3. TG and DSC curves of thermal decomposition of $(\text{CH}_3)_3\text{NHAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

From the TG and DSC curves of $(\text{CH}_3)_3\text{NHAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Fig.3) it can be concluded that the thermal decomposition of this compound is complicated and it is very difficult to resolve the dehydration process from the decomposition of the anhydrous double sulphate. Nevertheless, on a basis of the total mass loss at 323° , where a short level of 55.16 appears, and the calculated value for one mole of trimethylammonium sulphate and six moles of water $27.03 + 27.9 = 55.83$, and a mass of the residue at 700° of 15.39% (calculated value for Al_2O_3 , 13.39%) the stoichiometry of above compound was confirmed. More endothermic peaks up to 323° can be seen (on DSC curve) which indicate the dehydration and dissociation of double sulphate according to the equation:



As a consequence of thermal decomposition and a reduction process:



more exothermic maxima can be seen at higher temperatures.

The mass residue at 440° is 29.22% and the calculated value for $\text{Al}_2\text{O}_2\text{SO}_4$ is 29.20%. Above this temperature, the decomposition continues without remarkable effects on the DSC curve:



A difference in the mass of the obtained residue at 700° and the calculated value for Al_2O_3 of about 2.2% (Table 1) is possibly due to the fact that the decomposition is not completely finished, as can be seen from the TG curve.

The stoichiometry of II – $[(\text{CH}_3)_3\text{NH}]_3\text{Al}(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ was established by means of elemental analysis and igniting of the compound at 900° (Table 1). Different types of compounds of the same M(III) and the same monovalent cation is a frequent occurrence, e.g. Fe(III) [12] and Ln(III) [11].

By synthesis of double sulphate of Al(III) with tetramethylammonium, the compound $(\text{CH}_3)_4\text{NAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained in a molar ratio of 1:4. The stoichiometry of this compound was confirmed by means of elemental and thermal analysis in an air and nitrogen atmosphere (Table 1). As can be seen from Fig. 1a, TG, DTG and DTA curves indicate a thermal decomposition in two well resolved stages. In the 1st stage gradual evolution of water takes place. The mass loss at this stage (from 20 to 280°) is 26.11, calculated value for six moles of water 26.94%. The second stage of thermal decomposition begins at 300 and involves more steps, connected with endothermic and exothermic effects. This points to the possibility of the formation of intermediary products. Because this stage takes place at a narrow temperature interval, it is very difficult to resolve it. In the 1st step of the 2nd stage, which is from 300 to 386° , trimethylamine is liberated. The mass loss in this step is 14.7, calculated value 14.73%. In the 3rd step aluminium(III) sulphate decomposes.

Thermal decomposition takes place as:

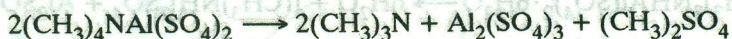
First stage ($20 - 280^\circ$)



mass loss: obtained 26.11, calculated for six moles of water 26.94%.

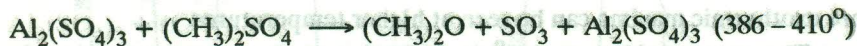
Second stage ($300 - 600$)

1st step ($300 - 386^\circ$)



mass loss 14.10, calculated for trimethylamine 14.73%.

2nd step ($386 - 410^\circ$)



mass loss 16.80, calculated for dimethyl ether and SO_3 15.71%.

Above this temperature, the thermal decomposition continues to:



and partially to:



mass loss 30.4, calculated value if $\text{Al}_2\text{O}(\text{SO}_4)_2$ is obtained 26.92%.

Thermal decomposition of $(\text{CH}_3)_4\text{NAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a nitrogen atmosphere (Fig.1b) points to a different thermal decomposition in the 2nd stage versus that in air. As a final product Al_2O_3 was obtained (mass of the residue 11.95, calculated value 12.70%. This stage is related to a more endothermic and exothermic effect (see DTA curve Fig.2b). In the 1st step of this stage (from 300 to 410°), from the mass loss of 33.00% it can be concluded that liberation of trimethyl amine, dimethyl ether and SO_3 takes place according the equation:



In the 2nd step aluminium(III) sulphate decomposes in the presence of the liberated carbon to aluminium(III) oxide.

By a synthesis of double sulphate of Al(III) with diethylammonium, only a compound with an empirical formula $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained. This empirical formula was established by elemental and TG analysis and determination of aluminium(III) oxide by ignition of the double sulphate at 900° (see Table 1).

TG, DTG and DTA curves (Fig. 2a) show that thermal decomposition of the above double sulphate takes place in two well resolved stages. In the 1st stage, from 40 to 260°, six moles of water are liberated (mass loss 26.83, calculated 26.94%). From 260° the 2nd stage of thermal decomposition begins which takes place in two steps. In the 1st step from 260 to 380°, dissociation of the anhydrous double sulphate with an endothermic maximum at 307° takes place:



mass loss 30.67, calculated 30.44%.

In the 2nd step aluminium(III)sulphate decomposes. The mass of residue of 16.02% indicates that a mixture of $\text{Al}_2\text{O}_2\text{SO}_4$ (calculated value 22.67%) and Al_2O_3 (calculated value 12.7%) was obtained.

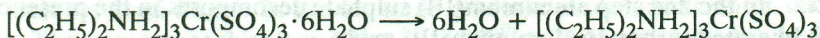
By synthesis of double sulphate of chromium(III) with diethylammonium, a compound with the empirical formula $[(\text{C}_2\text{H}_5)_2\text{NH}_2]_3\text{Cr}(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ was obtained. This empirical formula was established by elemental and thermal analysis. This formula is different from that of aluminium(III) double sulphate with the same (diethylammonium) monovalent cation.

Thermal decomposition of the above compound (Fig. 2b) takes place in two well resolved stages. In the 1st stage, from 40 to 190° a dehydration process with a different rate (more DTG maxima), takes place. The mass loss is 16.4%, calculated value for six moles of water 16.12%. In the 2nd stage more well resolved steps can be seen. In the 1st step, from 200 to 375° with endothermic

maximum at 282°, one mole of diethylammonium sulphate (a mass loss 36.63, calculated value 36.43%) is liberated and a sample of double sulphate is formed. In the 2nd step, from 375 to 500°, related to the exothermic maximum at 450°, chromium(III) sulphate is formed with the liberation of diethylammonium sulphate (a mass loss 18.77%, calculated value 18.22%. In the 3rd step chromium(III) sulphate decomposes in the presence of liberated carbon [10] to Cr₂O₂SO₄ (the mass of residue is 9.7%, calculated value 11.93%).

The thermal decomposition can be expressed as follows:

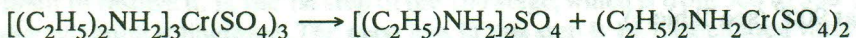
First stage (40 – 190°)



mass loss 16.40%, calculated value 16.48%

Second stage (200 – 800°)

1st step (200 – 375°)



mass loss 36.63%, calculated value 36.43%

2nd step (375 – 500°)



mass loss 18.77%, calculated value 18.22%

3rd step (above 500°)



mass of residue 9.7%, calculated value 11.93%.

As can be seen from Table 1, all double sulphates of Al(III) are hexahydrates like the double sulphate with dimethylammonium [9] and with other monovalent cations [1]. Double sulphate crystalohydrates of Al(III) with monovalent cations with less than six molecules of water in one formula unit, obtained by crystallisation from water solutions, are not known up to now. This fact leads us to the conclusion that the normal coordination of Al(III) in double sulphate crystalohydrates is an octahedron, formed from six molecules of water, as is presented in Al(III) alums [1–6] and found in dimethylammonium aluminum(III) sulphate hexahydrate [13].

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ВЕРА ЈОРДАНОВСКА

СИНТЕЗА, ИДЕНТИФИКАЦИЈА И ТЕРМИЧКО РАЗЛОЖУВАЊЕ
НА НЕКОИ ДВОЈНИ СУЛФАТИ НА $Al(III)$ И $Cr(III)$
СО АЛКИЛАМОНИУМ КАТЈОНИ

(Резиме)

При испарување на собна температура на водена смеса од метал(III) сулфат и алкиламониум сулфат се добиваат двојни сулфати кристалохидрати. Стехиометријата на двојните сулфати беше определена со помош на елементарна и термичка анализа, како и со определување на метал(III) оксидот при спалување на двојниот сулфат на 900° .

TG, DTG, DTA и DSC кривите добиени при динамички услови покажаа дека термичкото разложување на двојните сулфати е многу комплексно и дека се образуваат повеќе меѓупродукти. Сите двојни сулфати се хексахидрати иако односите на металниот и алкиламониум катјонот варираат. Тоа наведува на претпоставката дека веројатно металниот катјон е опкружен со шест молекули вода на ист начин како при стипсите.

Institute of Chemistry, Faculty of Sciences
The "Kiril i Metodij" University,
91000 Skopje, Macedonia