

VERA JORDANOVSKA

## THERMAL DECOMPOSITION OF SOME DOUBLE SULFATES OF IRON(III) WITH METHYLAMMONIUM IONS IN AIR AND IN AN INERT ATMOSPHERE

**Abstract:** Some new double sulfates of iron(III) with monomethyl-, dimethyl- and trimethylammonium cations were obtained by the reaction of iron(III) sulfate and methyl ammonium sulfates in the presence of sulfuric acid. Depending on the molar ration and the amount of sulfuric acid, different double sulfates with the same monovalent cations are obtained.

Thermal analysis in air and nitrogen in dynamic conditions points out a difference in thermal decomposition from that in an inert atmosphere, iron(III) sulfate decomposes to iron(III) oxy-sulfates.

### INTRODUCTION

Double sulfates of M(III) with monovalent cations are a subject of many investigations. So, double sulfates of Al(III), Cr(III) and Fe(III) with alkali, thallium(I) and ammonium cations with the general empirical formula  $M(I)M(III)(SO_4)_2 \cdot 12H_2O$  belong to the well known group of alums. Double sulfates of M(III) with monomethylammonium also belong to the above class of compounds [1, 2]. The crystal structure and dimorphism of alums [2, 3, 4, 5, 6, 7] as well as some physical properties such as dielectric and elastic constants, hardness, thermal stretching and thermoelastic behavior were also studied [2]. Thermal decomposition of Al-alums was investigated [8]. Thermal and magnetic properties of ferric methyl ammonium sulfate dodecahydrate [9], as well as its thermal decomposition, were also studied [12]. There are, also, a few data on double sulfates of M(III) with other methyl ammonium cations. The results of thermal decomposition of isomorphous aluminum and chromium dimethylammonium sulfates hexahydrates are given, recently [10]. A difference in thermal decomposition of these compounds in air and an inert atmosphere was evidenced. Also, a difference in thermal decomposition of double sulfates of some rare earths (III) and methyl ammonium cations were studied earlier [11].

This paper presents the results of synthesis and a thermal decomposition in dynamic conditions of some new iron(III) double sulfates with monomethyl-, dimethyl- and trimethylammonium cations in air and an inert atmosphere. These investigations are a continuation of our long term work on double sulfates of trivalent and monovalent cations.

## EXPERIMENTAL

### *Procedure and methods*

Double sulfates of iron(III) with methyl ammonium cations were obtained by evaporation at room temperature of a concentrated aqueous solution of iron(III) sulfate (0.0025 moles) and methylammonium sulfate in molar ratio from 1 : 4 to 1 : 13 in the presence of sulfuric acid (0.004 or 0.008 moles). The obtained crystalline products were filtered off, washed with ethanol and dried on air. For identification of the products obtained, X-ray powder diffraction patterns were carried out (they are not presented). For determination of their stoichiometry, elemental and thermal analyses were made. The results are given in Table 1.

Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves in an air atmosphere were obtained on the Mettler Thermoanalyser in a flow of dry air with a rate of 5L/h, at a temperature interval from 20° to 600°; Pt/Pt-Rh thermocouple, Pt-crucibles (TD<sub>1</sub>), heating rate 6°/min, reference substance  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

TG and DTA curves in an inert atmosphere were done on Netzsch Thermoanalyser M STA 429 in a flow of dry nitrogen, Pt/Pt-Rh thermocouple, quartz crucibles, sample mass approximately 30 mg; heating rate 2°/min at a temperature interval from 20 to 500 and 600°. The reference substance for DTA determinations was  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

## RESULTS AND DISCUSSION

By the synthesis of a double sulfate of iron(III) with monomethylammonium, depending of the amount of sulfuric acid in the reaction mixture, two kinds of crystalhydrates were obtained. By means of elemental and thermal analysis, it was found that, CH<sub>3</sub>NH<sub>3</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O was obtained in the presence of lower concentration of sulfuric acid, and CH<sub>3</sub>NH<sub>3</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 3.5H<sub>2</sub>O in higher concentration (Table 1). Neither compound is an alum.

As can be seen from Fig. 1-1, the thermal decomposition of CH<sub>3</sub>NH<sub>3</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 3.5H<sub>2</sub>O in a flow of air proceeds in two stages. In the 1st stage, from 40 to 210°, a dehydration of the double salt takes place, and two endothermic maxima at 125° and 175° appear (see DTA curve). Two steps in this stage point out the graduate evaluation of water: in the 1st step, from 40° to 140°, the compound loses three moles of water (mass

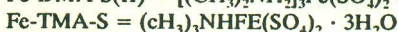
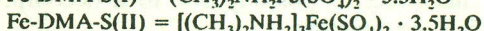
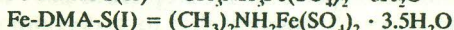
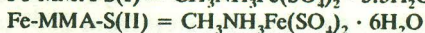
Table 1

*Results of elemental and thermal analysis of double sulfates of iron(III) with methylammonium cations*

%	Fe-MMA-S(I) (343.00) (1 : 4)	Fe-DMA-S(I) (357.02) (1 : 4)	Fe-TMA-S (361.96) (1 : 13)
C	3.52(3.50)	6.57(6.72)	10.61(9.95)
H	3.62(3.82)	3.63(4.24)	4.30(4.42)
N	4.35(4.08)	4.05(3.90)	4.37(3.87)
Fe	16.12(16.28)	14.63(15.64)	14.85(15.42)
Fe <sub>2</sub> O <sub>3</sub>	23.04(23.28)	(22.36)	21.23(22.06)
H <sub>2</sub> O	19.01(18.38)	15.22(17.66)	14.19(14.92)
		16.90*	14.30*
R <sub>2</sub> SO <sub>4</sub>	20.89(23.34)	29.58(26.36)	38.48(29.87)
Fe <sub>2</sub> SO <sub>4</sub>	60.10(58.28)	55.20(55.98)	47.33(55.22)
		44.50*	42.40*

	Fe-MMA-S(II) (387.93) (1 : 4)	Fe-DMA-S(II) (545.22) (1 : 8)
C		12.80(13.22)
H		5.55(5.73)
N		7.23(7.71)
Fe		10.60(10.25)
Fe <sub>2</sub> O <sub>3</sub>		15.15(14.65)
H <sub>2</sub> O	27.95*(27.84)	
R <sub>2</sub> SO <sub>4</sub>	19.65*(20.64)	
Fe <sub>2</sub> SO <sub>4</sub>	45.85*(51.52)	
Fe <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub>	(41.21)	



Calculated values are given in brackets.

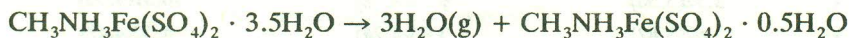
\* Obtained values in nitrogen.

loss 16.17, calculated value 15.73%) and in the 2nd step, an other 0.5 moles. The 2nd stage of thermal decomposition of anhydrous double sulfate takes place in more steps. In the 1st step from 210° up to 330° (DTG maximum at 304°) it possibly loses monomethylamine (mass loss 7.93, calculated value 9.05%) and in the 2nd loses sulfuric acid (mass loss 13%,

calculated value 14.29%) connected with an exothermic maximum at 377°. This means that this step is connected with the stabilization of iron(III) sulfate. As a final product at 600° iron(III) sulfate was obtained (the residue, 59.1, calculated value 58.28%). The thermal decomposition can be expressed with:

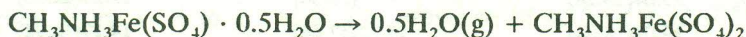
*First stage*

*1st step (40–140°)*



Mass loss: obtained from TG curve 16.17, calculated value 15.73%.

*2nd step (140–210°)*



Mass loss: obtained from TG curve 2.84, calculated 2.63%.

*Second stage*

*1st step (210–330)*



Mass loss: obtained 7.93, calculated 9.05%

*2nd step (330–430°)*



Mass loss: obtained 13.00%, calculated value 14.29%.

Thermal decomposition of monomethylammonium iron(III) sulfate hexahydrate in a nitrogen atmosphere (Fig. 2-1) takes place, also, in two well resolved stages. In the 1st stage the dehydration process, from 75° up to 210°, involved more steps. This means that evaluation of water takes place with a different rate (see DTG curve). The mass loss in this stage is 27.95, calculated value for six moles of water 27.84%. The 2nd stage of thermal decomposition of anhydrous double sulfate proceeds in two well resolved steps. The 1st step from 250° to 350°, connected with an endothermic effect, is possibly due to a decomposition of the double sulfate according to the reaction:



Mass loss: obtained 9.26, calculated 10.32%.

2nd step, from 370° to 450°, is connected with more exothermic effects which are possibly due to the formation of intermediate products. The total mass loss at 500° is 54.6%, which is greater than the calculated

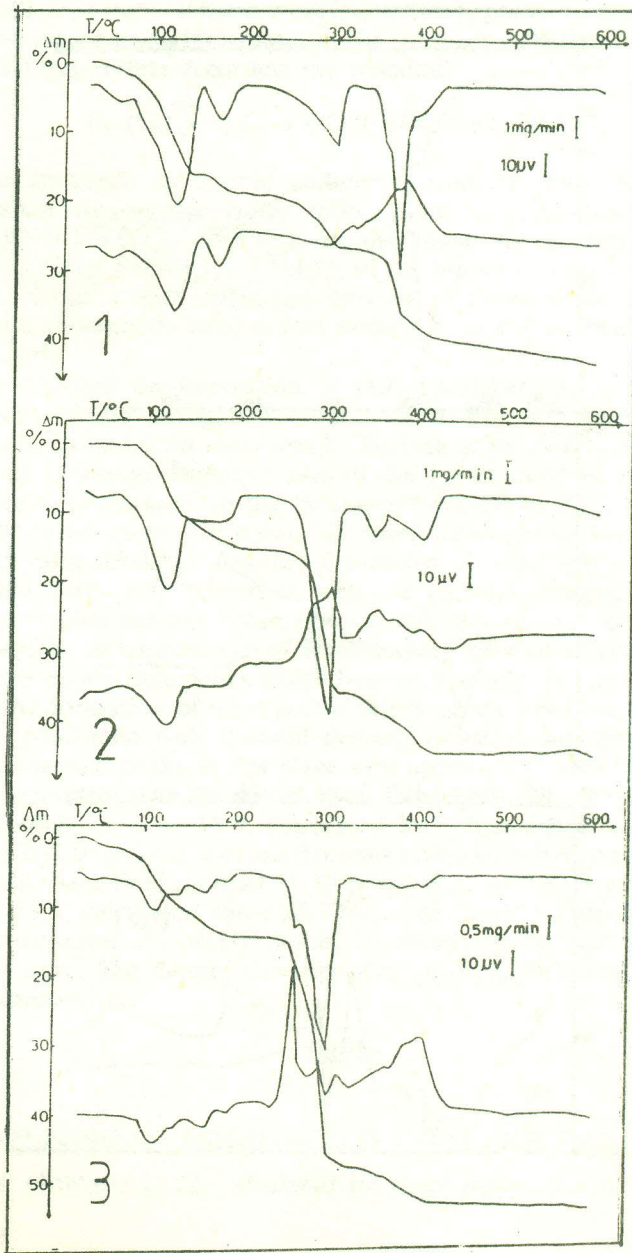


Fig. 1 - TG, DTG and DTA curves of thermal decomposition of:  
 1.  $\text{CH}_3\text{NH}_3\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ ; 2.  $(\text{CH}_3)_2\text{NH}_2\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ ;  
 3.  $(\text{CH}_3)_3\text{NHFe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in air.

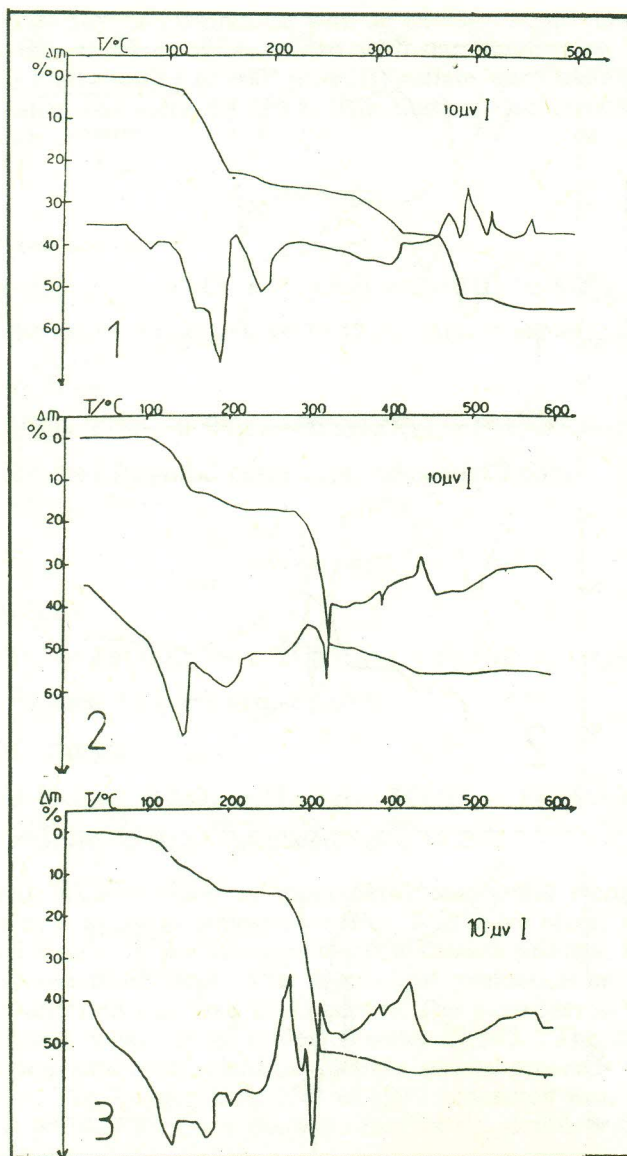
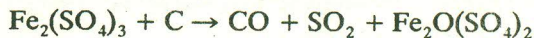


Fig. 2 - TG and DTA curves of thermal decomposition of:  
 1.  $\text{CH}_3\text{NH}_3\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; 2.  $(\text{CH}_3)_2\text{NH}_2\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ ;  
 3.  $(\text{CH}_3)_3\text{NHFe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  in nitrogen.

value 48.48% (if the residue is iron(III) sulfate), points to the possibility of decomposition of iron(III) sulfate, in the presence of liberated carbon [11], to iron(III) oxy-sulfate according the reaction:



The synthesis of double sulfate of iron(III) and dimethylammonium, depending on the molar ratio, yields two different compounds: I -  $(\text{CH}_3)_2\text{NH}_2\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ , in the lower molar ratio (1 : 4) and II -  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Fe}(\text{SO}_4)_3 \cdot 3.5\text{H}_2\text{O}$ , in the higher molar ratio (1 : 8) were obtained. X-ray powder diffraction patterns of I-compound and of its analogues with monomethylammonium point out to its identical structure (to be published).

The thermal decomposition of  $(\text{CH}_3)_2\text{NH}_2\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$  in an air atmosphere and nitrogen was undertaken. For II-compound only elemental analysis and total mass loss by heating at temperature of 900° were determined. Thermal decomposition of the I-compound in air, (Fig. 1-2), takes place in two stages. In the 1st stage, from 80° to 200°, the compound loses only three moles of water: obtained value from TG curve 14.64, calculated value 15.22%. Another 0.5 moles of water are lost in the 2nd stage, from 240°-430°, together with the thermal decomposition of the anhydrous double sulfate. More steps in this stage point out the graduate decomposition and formation of intermediary products. The DTA curve shows more exothermic peaks which belong, possibly, to the oxidation process and the formation of more stable intermediary products. The last conclusion is confirmed with thermal decomposition in nitrogen (Fig. 2-2) where exothermic peaks in this stage also appear. TG and DTG curves in nitrogen, point out that the dehydration finished in the 1st stage from 100° to 220° (obtained value 16.9, calculated for 3.5 moles of water 17.66%) and in the 2nd stage only thermal decomposition of anhydrous double sulfate proceeds. As a final product  $\text{Fe}_2\text{O}(\text{SO}_4)_2$  is obtained (obtained value for mass loss 55.5, calculated value 55.22%). This could be attributed to thermal decomposition of iron(III) sulfate by means of liberated carbon as was proposed before. The thermal decomposition of  $(\text{CH}_3)_2\text{NH}_2\text{Fe}(\text{SO}_4)_2 \cdot 3.5\text{H}_2\text{O}$  can be expressed as:

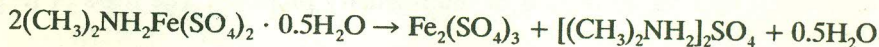
*In air:*

*1st stage,*



Mass loss: obtained 15.22, calculated for three moles of water 15.14%.

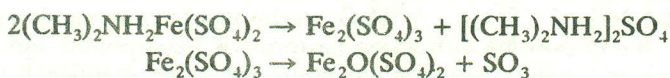
*2nd stage*



Mass loss: 29.58, calculated value only for dimethylammonium sulfate 26.36%, and with 0.5 moles of water 28.88%.

*In nitrogen,**1st stage*

Mass loss: 16.9, calculated 17.66%,

*2nd stage*

The mass of the residue at 500° was 44.5, calculated for  $\text{Fe}_2\text{O}(\text{SO}_4)_2$  is 44.78%.

With elemental analysis and total mass loss at 900° and determination of iron(III) oxide as the final product (see Table 1) of the product, obtained in molar ratio 1 : 8, the empirical formula  $[(\text{CH}_3)_2\text{NH}_2]_3\text{Fe}(\text{SO}_4)_3 \cdot 3.5\text{H}_2\text{O}$  was established. Two or more different structures of double sulfates of iron(III) with the same monovalent cation are not unknown. So, by the synthesis of double sulfates of Ln(III) with trimethyl ammonium, two types of compounds with different stoichiometry were obtained (in press).

By the synthesis of double sulfate of iron(III) with trimethylammonium, the double sulfate  $(\text{CH}_3)_3\text{NHFe}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$  was obtained. TG, DTG and DTA curves of thermal decomposition in air are given in Fig. 1-3. As can be seen, the thermal decomposition takes place in two well resolved stages. In the 1st stage, from 35° to 200°, in connection with the dehydration process, three moles of water are lost at different rates (see more DTG maxima on DTG curve). In the 2nd stage of thermal decomposition, from 250° to 420°, anhydrous double sulfate decomposes. More steps point out graduate decomposition and the formation of intermediary products. As final products at 600° mainly iron(III) oxy-sulfate and a small part of iron(III) sulfate were obtained (the mass of residue 47.33 and calculated value for iron(III) oxy-sulfate, 44.16%).

The thermal decomposition of the above compound in nitrogen (Fig. 2-3) takes place also in two stages. The dehydration, the 1st stage, is in the same temperature interval as in air (mass loss is 14.30%, calculated value for three moles of water, 14.92%). In the 2nd stage there is a difference in thermal decomposition of anhydrous double sulfate in comparison to that in air. So, at 600° as a final product mainly  $\text{Fe}_2\text{O}(\text{SO}_4)_2$  and a small part of  $\text{Fe}_2\text{O}_2\text{SO}_4$  were obtained. More endothermic and exothermic peaks in this stage confirmed the formation of intermediary products. The mass of residue is 42.40%.

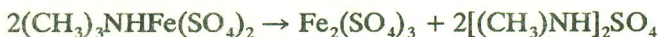
The thermal decomposition of double sulfate of iron(III) with trimethylammonium can be expressed as:



*1st stage in air and in nitrogen (30–210°)*



*2nd stage in air and nitrogen (250–440°)*



$\text{Fe}_2(\text{SO}_4)_3 + \text{C} = \text{Fe}_2\text{O}(\text{SO}_4)_2 + \text{SO}_2 + \text{CO}$  in nitrogen partially decomposed according the reaction:



The mass of residue 42.40, calculated for  $\text{Fe}_2\text{O}(\text{SO}_4)_2$  44.16%.

It seems that in all cases of thermal decomposition, in a nitrogen atmosphere, the thermal decomposition of iron(III) sulfate takes place by means of liberated carbon (product of the thermal decomposition of methylammonium sulfates) and  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ , as a final product at 600°, is obtained. In air iron(III) sulfate is stable up to 600°, but in the case of double sulfate with trimethylammonium, iron(III) sulfate, in the presence of a higher quantity of liberated carbon, it partially decomposes to  $\text{Fe}_2\text{O}(\text{SO}_4)_2$  starting from 300° and in nitrogen continues partially to  $\text{Fe}_2\text{O}_2\text{SO}_4$ . This is in agreement with earlier findings for the thermal decomposition of double sulfates of Ln(III) with methylammonium cations in an argon and an air atmosphere [11].

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ВЕРА ЈОРДАНОВСКА

ТЕРМИЧКО РАЗЛОЖУВАЊЕ НА НЕКОИ ДВОЈНИ СУЛФАТИ  
НА ЖЕЛЕЗО(III) СО МЕТИЛАМОНИУМ ЈОНИТЕ ВО ВОЗДУХ И  
ВО ИНЕРТНА СРЕДИНА

(Резиме)

Двојни сулфати на железо(III) со монометил-, диметил- и триметиламониум катјоните беа добиени при реакција на железо(III) сулфат и метил амониум сулфат во присуство на сулфурна киселина. Зависно од моларниот однос и количеството на сулфурна киселина, се добиени различни двојни сулфати со исти моновалентни катјони.

Термичката анализа во воздух и во азот во динамички услови покажа разлика во термичкото разложување и дека во инертна атмосфера разложувањето на железо(III) сулфатот продолжува до образување на железо(III) оксисулфати.

Institute of Chemistry,  
University of Skopje,  
91000 Skopje, Yugoslavia