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Synthesis, identification and thermal decomposition of double sulfates of Al(III) and Fe(III) with the ethanolammonium cation

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Abstract

By evaporation of an aqueous mixture of M(III) sulfate and ethanolammonium sulfate (a) in the presence of sulfuric acid and (b) without sulfuric acid, double acid, double sulfates of Al(III) and Fe(III) were obtained. The stoichiometries of the compounds were obtained by means of elemental and TG analyses. From the X-ray powder diffraction patterns it was concluded that, depending on the presence or otherwise of sulfuric acid, two different structures of the Al double sulfate with the same empirical formula $HOCH_2CH_2NH_3Al(SO)_4)_2 \cdot 6H_2O$ were obtained. It was also established from the TG curve that the $HOCH_2CH_2NH_3Fe(SO_4)_2 \cdot 2H_2O$ obtained dehydrates at a higher temperature and is more stable than the Al(III) double sulfates.

INTRODUCTION

Double sulfates of Al(III), Cr(III) and Fe(III) with monovalent cations with the general empirical formula $M(I)M(III)(SO_4)_2 \cdot 12H_2O$ belong to the well known group of alums. The double sulfates with monomethylammonium also belong to the alums [1,2]. The crystal structure and dimorphism of alums [2–7] and some physical properties have also been studied [2]. The thermal properties of Al(III) alums [8] and thermal and magnetic properties of Fe(III) methylammonium sulfate dodecahydrate [9] and its thermal decomposition have also been studied [10]. There are also some data on the synthesis and thermal decomposition of Al(III), Cr(III) and Fe(III) with various alkylammonium cations, such as methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium and diethylammonium [11–13], where stoichiometry is different from that of the alums. The crystal structures of the isomorphous double sulfates of Al(III) and Cr(III) with dimethylammonium have recently been presented [14].

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In this paper the results of the synthesis are presented, with the identification and thermal decomposition in static conditions of double sulfates of Al(III) and Fe(III) with the ethanolammonium monovalent cation. These investigations are a continuation of our long standing work on double sulfates of M(II) and M(III) with various nonclassical monovalent cations.

EXPERIMENTAL

Procedures and methods

Double sulfates of Al(III) and Fe(III) with ethanolammonium were obtained by evaporation at room temperature of a concentrated aqueous solution of M(III) sulfate (0.0025 mol) and ethanolammonium sulfate, in the molar ratio 1:4 for Al compounds and 1:8 for Fe compound, with addition of sulfuric acid (0.008 mol). The concentrated solution of ethanol ammonium sulfate was obtained by neutralization of 2-ethanolamine (Merck, Purum) with diluted sulfuric acid stepwise to pH 4 with a permanent cooling of the reaction mixture in ice–water. The other Al compound was obtained as above without addition on sulfuric acid. The crystalline products obtained were filtered off, washed with ethanol and dried in an exicator. For identification of the products obtained, X-ray powder diffraction patterns were obtained. For determination of their stoichiometries, elemental, TG and DT were performed. The results are given in Table 1.

Thermogravimetric (TG) analyses were performed using a Cahn RG Electrobalance in air atmosphere at a heating rate of 5°C min^{-1} over the range 20–900°C and using 10–12 mg of sample in a quartz crucible. The DTA was performed using a Netzsch differential thermal analyzer. DTA curves were obtained in static air atmosphere with samples masses of 70–100 mg at a heating rate of 5°C min^{-1} from ambient temperature to 900°C. The reference compound was pure alumina. The DTA peak

TABLE 1

Results of elemental and thermal analyses of the double sulfates of aluminum(III) and iron(III) with ethanolammonium [a]

	$RHAl(SO_4)_2 \cdot 6H_2O$ [b]	$RHAl(SO_4)_2 \cdot 6H_2O$ [b]	$RHFe(SO_4)_2 \cdot 2H_2O$ [c]
C	6.80 (6.17)	6.54 (6.17)	6.60 (6.94)
H	5.60 (5.18)	5.63 (5.18)	3.39 (3.50)
N	3.34 (3.60)	3.37 (3.60)	3.85 (4.50)
H_2O	28.02 (27.77)	29.67 (27.77)	10.61 (10.41)
M_2O_3	11.04 (13.10)	11.17 (13.10)	22.70 (23.07)

[a] The calculated values are given in parenthesis. [b] $M_r = 389.29$. [c] $M_r = 346.09$.

maxima were obtained at different temperatures from those found on the TGA curve because of the different furnace conditions and sample masses employed.

The X-ray powder diffraction patterns were recorded on a Philips PW 1050 vertical goniometer with a proportional counter using graphite monochromatized Cu Kα radiation.

RESULTS AND DISCUSSION

The X-ray powder diffraction patterns of the compounds obtained indicate their different crystal structures. Depending on the presence or otherwise of sulfuric acid in the reaction mixtures, two structurally different Al(III) double sulfates with general empirical formula $HOCH_2CH_2NH_3Al(SO_4)_2 \cdot 6H_2O$ (Table 1) were obtained. This finding of dimorphism is not new for Al compounds. The double sulfate of iron(III) obtained is a dihydrate. Further, depending on the concentration of sulfuric acid, two structurally different double sulfates of Al(III) with dimethylammonium [13, 15] are obtained. The difference in their structures has some influence on their thermal decomposition, as can be seen from Fig. 1. The three steps of thermal decomposition are better resolved

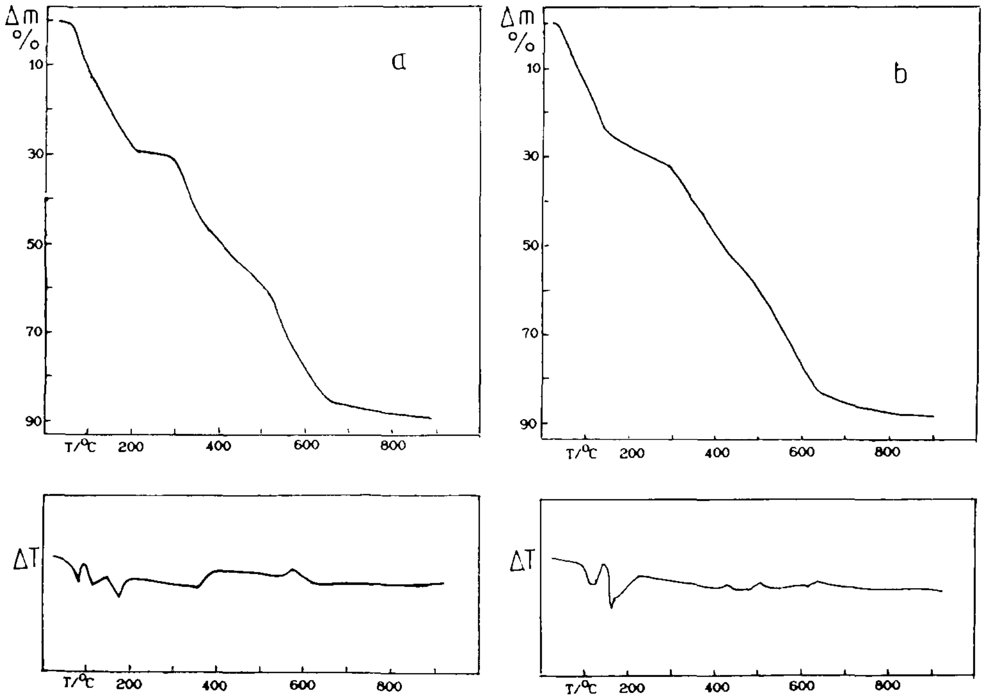

Fig. 1. TG and DTA curves of $HOCH_2CH_2NH_3Al(SO_4)_2 \cdot 6H_2O$ obtained (a) without addition of sulfuric acid and (b) with addition of sulfuric acid.

in the case of the compound obtained without sulfuric acid (Fig. 1a) than in the other compound obtained in the presence of sulfuric acid (Fig. 1b). The thermal decomposition of both compounds is described below with the following equations.

$HOCH_2CH_2NH_3Al(SO_4)_2 \cdot 6H_2O$ ($M_r = 389.29$)

Compound obtained without addition of sulfuric acid (Fig. 1a)

Step 1 (42–225°C)

$RHAl(SO_4)_2 \cdot 6H_2O \rightarrow 6H_2O + RHAl(SO_4)_2$ ($R = HOCH_2CH_2NH_2$)

Mass loss: found, 28.02%; calculated, 27.77%

Step 2 (225–488°C)

$2RHAl(SO_4)_2 \rightarrow (RH)_2SO_4 + Al_2(SO_4)_3$

Mass loss: found, 28.89%; calculated, 28.29%

Step 3 (488–906°C)

$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$

Mass loss: found, 32.05%; calculated, 30.85%.

Compound obtained with addition of sulfuric acid (Fig. 1b)

Step 1 (34–219°C)

$RHAl(SO_4)_2 \cdot 6H_2O \rightarrow 6H_2O + RHAl(SO_4)_2$

Mass loss: found, 28.29%; calculated, 27.77%.

Step 2 (219–488°C)

$2RHAl(SO_4)_2 \rightarrow Al_2(SO_4)_2 + (RH)_2SO_4$

Mass loss: found 29.67%; calculated, 28.29%.

Step 3 (488–900°C)

$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$

Mass loss: found, 30.87%; calculated, 30.85%.

γ-Aluminum(III) oxide is obtained as final product from both compounds, which is confirmed by the X-ray powder Diffraction patterns (Powder diffraction File No. 10-425 [16]).

Because on the DTA curve for step 1 three endothermic peaks can be seen in Fig. 1a and only two in Fig. 1b, it could be supposed that the water in these compounds is connected to Al(III) in different ways. In the known aluminum double sulfate crystallohydrates there are six water molecules in the coordination sphere of Al(III) [2,3,6,8,14]. Steps 2 and 3 of the thermal decomposition of the anhydrous salts are not well resolved. On the DTA curves more peaks can be seen and it could be concluded that this process involves more thermal effects.

$HOCH_2CH_2NH_3Fe(SO_4)_2 \cdot 2H_2O$ (M_r = 345.99)

The thermal decomposition of this compound takes place in three well resolved steps (Fig. 2). In step 1, the dehydration of the compound occurs in one step. In step 2, the anhydrous double salt decomposes via iron(III) sulfate to iron(III) oxisulfate. In step 3 this decomposes to iron(III) oxide. These reactions are described by the following equations.

Step 1 (114–219°C)

$$RHFe(SO_4)_2 \cdot 2H_2O \rightarrow 2H_2O + RHFe(SO_4)_2$$

Mass loss: found, 10.61%; calculated, 10.41%.

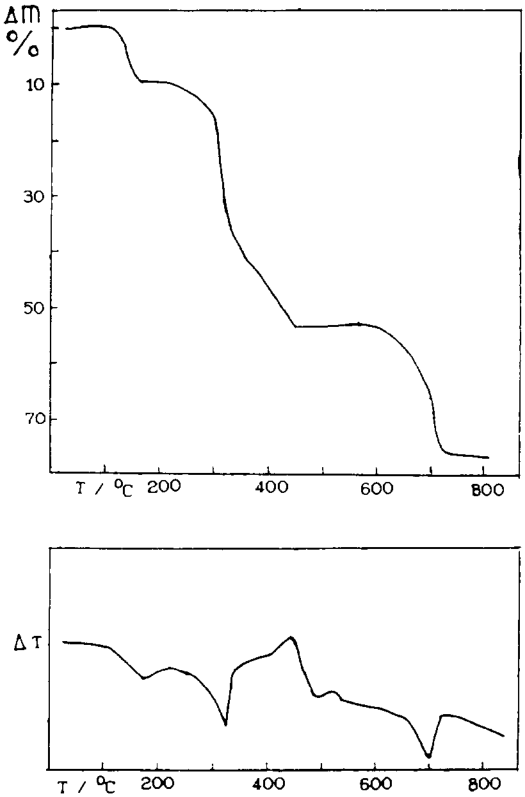

Fig. 2. TG and DTA curves of $HOCH_2CH_2NH_3Fe(SO_4)_2 \cdot 2H_2O$.

Step 2 (219–500°C)

$2RHFe(SO_4)_2 \rightarrow Fe_2(SO_4)_3 + (RH)_2SO_4$

$Fe_2(SO_4)_3 \rightarrow Fe_2O(SO_4)_2 + SO_3$

Mass loss: found, 42.78%; calculated, 43.40%.

Step 3 (608–829°C)

$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3$

Mass loss: found, 23.56%; calculated, 23.14%.

The formation of iron(III) oxisulfate is related to an exothermic peak at about 445°C. The endothermic peak at about 700°C is related to the decomposition of iron(III) oxisulfate to iron(III) oxide, which means that this is an endothermic process. The X-ray power diffraction pattern of the residue confirms that iron(III) oxide is obtained (File No. 13-534 [16]).

CONCLUSIONS

From the TG curves (Figs. 1 and 2) it can be inferred that the double sulfate hexahydrates of aluminum are less stable than the double sulfate dihydrate of iron(III) because they dehydrate at a lower temperature, whereas the stability of the anhydrous salts is similar. The double sulfate of aluminum obtained in the presence of sulfuric acid is less stable than that obtained without it.

Under the same conditions as described in the Experimental section, it was not possible to isolate a double sulfate of Cr(III) with ethanolammonium. In all attempts, only a viscous liquid was obtained.

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