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DOUBLE SULFATE OF IRON(III) WITH MONOVALENT TRIS(HYDROXYMETHYL) AMMONIUM METHANE TETRAHYDRATE AS ADDUCT WITH TRIS(HYDROXYMETHYL)AMINOMETHANE. SYNTHESIS, AND DETERMINATION OF ITS GENERAL FORMULA

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Abstract

By stepwise neutralization of reaction mixture of aqueous solution of Fe(III) sulfate and tris-(hydroxymethyl) aminomethane, in molar ratio 1:2, with diluted sulfuric acid up to dissolution of the obtained Fe(III) hydroxide, double sulfate as crystalline product was obtained. The stoichio-metry of the obtained compound was determined by means of elemental and TG analysis. It was characterized by their IR spectrum. It was found that the obtained compound is not pure double sulfate but is adduct with started amine and has a general empirical formula closed to $Fe(HOCH_2)_3CNH_3(SO_4)_2.4H_2O.(HOCH2)_3CNH_2$.

TG, DTG and DTA curves were done in static air atmosphere from room up to $1000^{\circ}C$. The stepwise dehydration (three DTG peaks in this temperature region) of the investigated compound points out that the four water molecules are bonded on a different way.

The thermal decomposition of the anhydrous compounds starts at about $210^{\circ}C$ and is very complex. This process takes place in many steps which are not well resolved.

Key words: iron, tris(hydroxymethyl)aminomethane, double sulfate, synthesis, identification, thermal decomposition.

Introduction

Double sulfates of M(III) with monovalent cations are a subject of many investigations. So, dou-ble sulfates of trivalent aluminium, chromium and iron with alkali, thallium(I) and ammonioum cations with the general empirical formula $M(I)M(III)(SO_4)_2.12H_2O$ belong to the well known group of alums. Double sulfates of above metals with monomethylammonium cation also belong to the above class of compounds [1,2]. The crystal structure and dimorphism of alums [2-7] as well as some physical properties such as dielectric and elastic constants, hardness, thermal stretching and thermoelastic behavior were also studied [2]. There are, also, a few data on the synthesis, identification and thermal behavior of double sulfates of trivalent aluminium, iron and chromium with other substituted ammonium monovalent cations as: dimethyl-, trimethyl-, tetra-methyl-, diethyl-, ethanol-, diethanol-, and triethanolammonium cations [8-12]. The coordination compounds of transition metals with 2-amino-2-hydroxymethylpropane-1,3-diol or tris(hydroxy-methyl)aminomethane are of great interest for bioinorganic chemistry. The use of aminoalchols to extract heavy metals from organisms is also known [13]. It is also presented coordination compounds of Cu(II) halides with tris(hydroxymethyl) aminomethane which are with fungicidal and herbicidal activity [14]. Resently, we have also present, the results of synthesis, cha-racterization by means of X-ray powder diffraction pattern and IR spectrum and TG. DTG, DTA, of double sulfate of aluminium with tris(hydroxymethyl)ammoniummethane[to be published].

As a continuation of our long standing work on double sulfates of M(III) with nonmetallic monovalent cations, in the present paper we report results of the investigations on the synthesis, identification and thermal decomposition of double sulfate of Fe(III) with tris(hydroxymethyl)am-

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moniummethane(I) with the nearest general empirical formula: $Fe(HOCH_2)_3CNH_3(SO_4)_2 \cdot 3H_2O$ $\cdot(HOCH_2)_3CNH_3$ for which we have found no data in the literature.

Experimental

Procedure for Synthesis

Double sulfate of Fe(III) with tris(hydroxymethyl)ammoniummethane is obtained by evaporation at ambient temperature of a concentrated aqueous solution of M(III)sulfate (0.004 mole) and trishydroxymethyl)amminomethane in molar ratio 1:2 and stepwise neutralized with diluted sulfuric acid to pH 5. The obtained crystalline products was filtered off, washed with ethanol-water, dried in air and characterized by elemental analyses and IR spectrum. The thermal behavior of the product was also investigated in temperature interval from ambient up to about 1000°C.

Analytical Method

TG, DTG and DTA curves were carried out with a Derivatograph Q (MOM,Hungary) in a static air atmosphere at a heating rate of 10°C min^{-1} over the range from room temperature up to 1000°C, using 100 mg sample in Pt crucibles. Sensitivity: TG 100 mg, DTG, 1 mV: DTA, 0.5 mV. The reference substance was pure alumina.

Results and Discussion

From the results of the elemental analysis as well as from the mass of water and residue, determined by TG analysis, it could be supposed the following general formula:

$$Fe(HOCH_2)_3CNH_3(SO_4)_2 \cdot 4H_2O \cdot (HOCH_2)_3CNH_2.$$
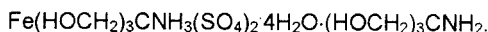
That means that the obtained compound is not pure double sulfate but in the same time iron is coordinated with amine.

Thermal Studies

The *TG, DTG* and *DTA* curves of the thermal decomposition of iron(III) double sulfate with tris(hydroxymethyl)ammoniummethane coordinated with tris(hydroxymethyl)amino methane is shown on Fig. 1.

The thermal decomposition of the double sulfate takes place in tree stages. The first stage, which related with the dehydration process is not well differentiated from the next stage and the calculation of the mass loss which correspond with water molecules is made on the basis of the shape of the DTA curve supported by the elemental analysis. The two DTG peaks (the biggest at 80°C) related to dehydration points out that water molecules go out stepwise in a large temperature interval (a large DTA endothermic pocket) from 40-210°C.

The decomposition of the anhydrous compound (the second stage) takes place continuously (three DTG peaks, the biggest at 225°C) with a high exothermic peak (DTA curve) at 435°C. This suggests that the decomposition is not only dissociation, but intensive redox process takes place (the organic part of the molecule). The value of the mass loss at 450°C points out that $Fe_2O(SO_4)_2$ is obtained (mass loss obtained 28.2; calculated 28.39%). This compound exist in a large temperature interval from 450-550°C.
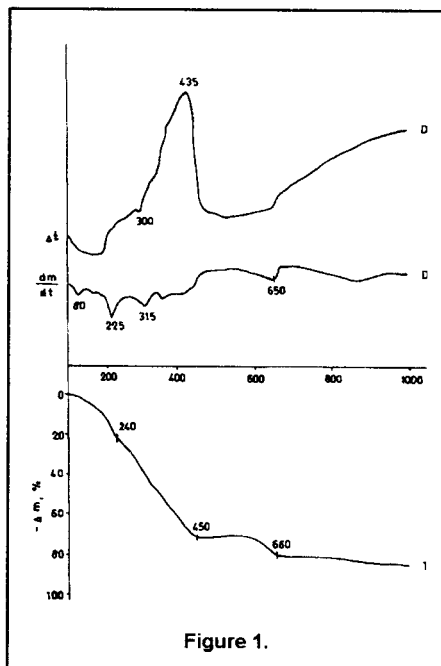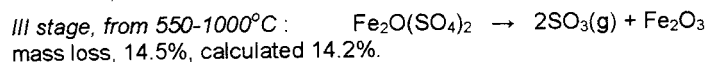

Figure 1.
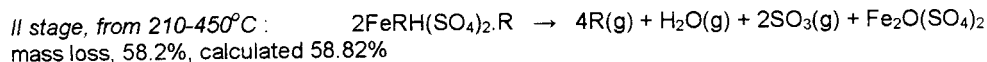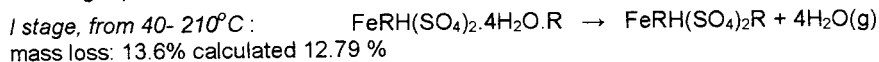
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The thirth stage is related with a decomposition of $Fe_2O(SO_4)_2$ and formation of Fe_2O_3 at temperature upper than 550°C. This process is connected with hardly remarkable DTA events. The formation of oxysulfates by thermal decomposition are also known by other iron double sulfates [11,12].

The thermal decomposition of the investigated compound could be presented with following equations: $R= (HOCH_2)_3CNH_2$:

I stage, from 40- 210°C : $FeRH(SO_4)_2.4H_2O.R \rightarrow FeRH(SO_4)_2R + 4H_2O(g)$
mass loss: 13.6% calculated 12.79 %

II stage, from 210-450°C : $2FeRH(SO_4)_2.R \rightarrow 4R(g) + H_2O(g) + 2SO_3(g) + Fe_2O(SO_4)_2$
mass loss, 58.2%, calculated 58.82%

III stage, from 550-1000°C : $Fe_2O(SO_4)_2 \rightarrow 2SO_3(g) + Fe_2O_3$
mass loss, 14.5%, calculated 14.2%.

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