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SYNTHESIS, CHARACTERISATION AND THERMAL DECOMPOSITION OF DOUBLE SULFATE

Al(III) and trishydroxymethyl-ammoniummethane

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Abstract

Upon evaporation at room temperature of an aqueous mixture containing Al(III) sulfate and trishydroxymethyl-ammoniummethane sulfate in a molar ratio 1:2, double sulfate as crystalline product was obtained. The stoichiometry of the obtained compound was determined by means of elemental and TG analysis. For identification, IR-spectra and X-ray powder diffraction patterns were done. It was found that the general formula of the obtained compound is $Al(HOCH_2)_3CNH_3(SO_4)_2{\cdot}6H_2O$. As revealed by TG, DTG and DTA analysis, the dehydration of the Al-compound takes place in one step which points out that the six water molecules are bonded in the same way. The thermal decomposition of the anhydrous compound starts at about 260°C and is very complex. This process takes place in many steps which are not well resolved. The pathway of the thermal decomposition is also supposed.

Keywords: derivatograph-Q, double sulfate of Al(III)

Introduction

Double sulfates of Al(III) with monovalent cations are a subject of many investigations. Thus, double sulfates of trivalent aluminium, chromium and iron with alkali metal cations, as well as with 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 the above metals with monomethylammonium cation also belong to the above-mentioned 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 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-, tetramethyl-, diethyl-, etha-

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nol-, diethanol-, triethanol and diisopropylammonium cations [8–13]. The crystal structure of double sulfate of trivalent Al with dimethylammonium has been determined and dimorphism of this compound has been established [14]. Recently, FTIR and polarized Raman spectra of dimethylammonium aluminium sulfate hexahydrate have been presented [15, 16].

As a continuation of our previous work on double sulfates of M(III) with non-metallic monovalent cations, in the present paper we report results of the investigations on the synthesis, identification and thermal decomposition of double sulfate of Al(III) with trishydroxymethyl ammoniummethane(I) with empirical formula:

$$\mathrm{Al(HOCH_2)_3CNH_3(SO_4)_2{\cdot}6H_2O}$$

for which we have found no data in literature.

It was our attempt to synthesize a double sulfate of chromium(III) with the same monovalent cation as well, but only viscous solutions was obtained.

Experimental

Chemicals

Trishydroxymethylaminomethane (Merck, p.a.), analytical grade aluminium for the preparation of aluminium sulfate solution (c=0.5 mol dm^{-3}), and sulfuric acid (p.a., Merck).

Procedure for synthesis

Double sulfate of Al(III) with trishydroxymethyl-ammonium methane was obtained by evaporation at ambient temperature of a concentrated aqueous solution of Al(III) sulfate (0.004 mole) and trishydroxymethylaminomethane in a molar ratio 1:2 and neutralized by a diluted sulfuric acid to pH 5. The obtained crystalline products were filtered off, washed with ethanol–water, dried in air, and characterized by elemental analyses, FTIR spectroscopy and X-ray powder diffraction patterns. The thermal behavior of the products was also investigated in temperature interval from ambient up to about 1000°C.

Analytical methods

Elemental analyses for carbon and hydrogen were carried out using Liebig's method and a carbon-hydrogen analyzer (Coleman Model 33); nitrogen was analyzed using Duma's method.

X-ray powder diffraction patterns were taken on a Philips PW 1050 Vertical Goniometer with proportional counter, using graphite-monochromatized CuK_α radiation.

Fourier-transform infrared (FTIR) spectra of the synthesized compound (KBr pellets) were recorded on a Perkin Elmer System 2000 FTIR interferometer at room (*RT*) and low temperature (*LT*, ~100 K), using a Graseby-specac variable temperature cell for low temperature measurements. Resolution of 4 cm^{-1} was used, averaging 64 scans at *LT* in order to obtain a good signal-to-noise ratio.

TG, DTG and DTA curves were recorded 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 1273 K, 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

Comparison of the X-ray powder diffraction pattern for the present compound (as well as of the IR spectra) with those of other aluminium double sulfates (with different alkylammonium cations) suggests that the investigated double sulfate appears with a substantially different structure. This points out that as in many other double sulfates the size ratio of both cations determined the crystal structure [17].

From the results of the elemental analysis as well as from the mass of water and residue, determined by thermogravimetry the following general formula could be supposed $Al(HOCH_2)_3CNH_3(SO_4)_2{\cdot}6H_2O$ (Elemental analyses: C, found 10.84, calculated 10.70%; H, found 5.57; calculated 5.38%; N, found 2.75; calculated 3.12%).

The above chemical formula suggests that, as in other Al double sulfates crystallohydrates, six water molecules are present which are most probably coordinated with Al(III) [1, 2, 14]. This was confirmed with IR spectra where only one sharp band from HOH stretching vibration appears.

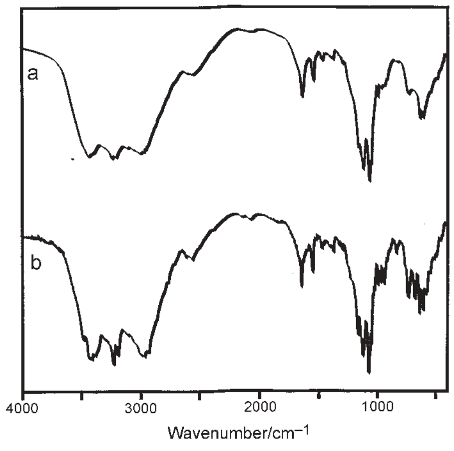

Fig. 1 a – *RT* and b – *LT* FTIR spectra of the investigated compound

RT and LT spectra of $Al(HOCH_2)_3CNH_3(SO_4)_2{\cdot}6H_2O$ are shown in Fig. 1. Since the crystal structure of the investigated compound has not been reported, we are unable to provide a more rigorous analysis of the IR spectral data which would be based on the full unit-cell group analysis. We, therefore, analyze the spectra semi-empirically, appealing on the most important characteristics of vibrational force fields in the case of structurally similar compounds/fragments. As can be seen, the region of N–H and O–H stretching modes of the present compound spans from ~3480 to ~3050 cm^{-1}. Such appearance indicates the presence of hydrogen bonds from medium to rather appreciable strength (possibly of both N–H···O and O–H···O type). We attribute the bands appearing somewhat below 3000 cm^{-1} (from ~2980 to 2920 cm^{-1}) to the aliphatic C–H stretchings. The appearance of a relatively sharp band due to HOH bending modes at ~1640 cm^{-1} implies a rather symmetrical arrangement of water molecules coordinated to Al^{3+} cation (although this may not be regarded as a final conclusion without more involved spectroscopic investigations). Bands appearing at somewhat lower frequencies (from ~1550 to ~1300 cm^{-1}) may be attributed to various NH and CH_2 bending modes. Most probably due to the NH bendings are the rather strong bands appearing at 1160 and 1117 cm^{-1}. One of the most intensive band multiplets in the whole spectrum (at ~1066 cm^{-1}) is due to the ν_3 mode (the antisymmetric stretching) of the SO_4^{2-} group. It is impossible to unambiguously state whether this multiplet of bands originates from the factor-group splitting of the SO_4^{2-} ν_3 vibration alone, or whether bands due to other groups in the structure overlay with this mode in the same spectral region. The same discussion is essentially valid for the group of bands appearing at somewhat lower frequencies (from ~986 to 930 cm^{-1}). The highest frequency band of these (appearing at ~986 cm^{-1}), which is rather sharp, may be attributed to the site or factor-group activated ν_1 mode of the SO_4^{2-} group (the totally symmetric vibration of a regular tetrahedron is IR forbidden by the selection rules for the T_d point group). The appreciable intensity of this mode in the spectrum of the present compound may be attributed to rather large deviation of the SO_4^{2-} group geometry from that of a regular tetrahedron. Lower frequency bands cannot be unambiguously assigned as they may originate from both HOH and NH librations and other modes as well.

Thermal studies

TG, DTG and DTA curves of the thermal decomposition of the title compound are presented in Fig. 2.

The thermal decomposition takes place in two stages (with more steps within the second stage). The first stage which is related to the dehydration of the compound takes place within a short temperature interval in a single step (DTG maximum at 120 and DTA at 125°C) which indicates that six water molecules are structurally equal as also implied by IR spectra. This stage is not well resolved (with a horizontal level) from the next stage, but differentiation is made by means of inflection point.

The decomposition of anhydrous double sulfate takes place in the temperature interval from 180 to 610°C without any level on the TG curve (the TG curve descents monotonically) followed by some weak DTA peaks and one remarkable exothermic peak at 585°C. Many thermal effects on the DTA curves lead us to the conclusion that this process is not only dissociation, but also an oxidation-reduction process. The fact that this process mainly ends at 610°C which is much lower than the corresponding process of pure aluminium sulfate [18] suggests that the presence of carbon liberated from organic cation decreases the temperature of aluminium sulfate dissociation, as it was noticed also by the thermal decomposition of other alkylammonium sulfates

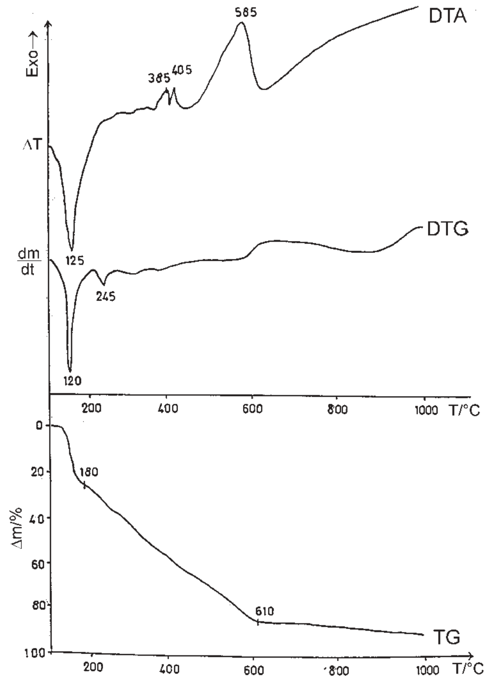

Fig. 2 TG, DTG and DTA curves for the investigated compound

[12]. Al_2O_3 as final product is obtained. The overall thermal decomposition could be presented with following equations:

I Stage, from 70–180°C:

$$Al(OHCH_2)_3CNH_3(SO_4)_2{\cdot}6H_2O \rightarrow Al(OHCH_2)_3CNH_3(SO_4)_2+6H_2O$$

mass loss: found 25.2%; calculated 24.06%.

II Stage, from 180–610°C:

$$2Al(OHCH_2)_3CNH_3(SO_4)_2 \rightarrow [(HOCH_2)_3CNH_3]_2SO_4+3SO_3+Al_2O_3$$

mass loss: found 63.0%; calculated 64.58%.

The attempt to obtain a double sulfate of Cr(III) with title compound was unsuccessful and only a viscose liquid was obtained. Investigations on the double sulfates of Fe(III) are in progress.

References

1 B. H. Serezhkin, 10 (1984) 20.
2 S. Haussuhl, Kristallography der Alaune, Z. Kristallogr. Mineral., 116 (1961) 371.
3 R. O. W. Fletcher and H. Steeple, Acta Crystallogr., 15 (1962) 960.

4 A. H. C. Ledsham and H. Steeple, Acta Crystallogr., Sect. B, 24 (1968) 320.
5 R. O. W. Fletcher and H. Steeple, Acta Crystallogr., 14 (1961) 891.
6 R. O. W. Fletcher and H. Steeple, Acta Crystallogr., 17 (1964) 290.
7 A. C. Larson and Don T. Cromer, Acta Crystallogr., 22 (1967) 793.
8 V. Jordanovska, Contrib. Mac. Acad. Sci. Arts, 12 (1991) 61.
9 V. Jordanovska, J. Thermal Anal., 35 (1989) 1331.
10 V. Jordanovska, Contrib. Mac. Acad. Sci. Arts, 13 (1992) 47.
11 V. Jordanovska and R. Trojko, Thermochim Acta, 228 (1993) 241.
12 V. Jordanovska, R. Trojko and B. Boyanov, Thermochim. Acta, 275 (1996) 301.
13 V. Jordanovska, B. Boyanov and P. Naumov, J. Therm. Anal. Cal., 66 (2001) 533.
14 N. Galesic and V. B. Jordanovska, Acta Cryst., C48 (1992) 256.
15 V. P. M. Pillai, V. U. Nayar and V. B. Jordanovska, Optics and Optoelectronic, 1 (1998) 193.
16 V. P. M. Pillai, V. U. Nayar and V. B. Jordanovska, Spectrochim. Acta, 56A (2000) 887.
17 V. Petrusevski and S. Aleksova, Croat. Chem. Acta, 64 (1991) 577.
18 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam 1963, p. 230.