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# SYNTHESIS, CHARACTERISATION AND THERMAL DECOMPOSITION OF DOUBLE SULPHATES OF Al AND Cr(III) WITH DIISOPROPYLAMMONIUM ION

*V. Jordanovska*[1], *B. Boyanov*[2] *and P. Naumov*[1]

[1]Institute of Chemistry, Faculty of Natural Science and Mathematics, University St. Cyril and Methodius, 91000 Skopje, Macedonia
[2]Faculty of Chemistry, Plovdiv University Paissii Hilendarski, 4025 Plovdiv, Bulgaria

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## Abstract

On evaporation at room temperature of an aqueous mixture of *M*(III) sulphate and diisopropylammonium sulphate in a molar ratio 1:3, double sulphates of Al and Cr as crystalline products were obtained. The stoichiometry of the obtained compounds was determined by means of elemental and TG analysis. The above compounds were characterized by their IR spectra and X-ray powder diffraction patterns, as well. It was found that they have a general empirical formula $M(CH_3CHCH_3)_2NH_2(SO_4)_2\cdot 6H_2O$ and that they are isostructural.

TG, DTG and DTA curves were done in static air atmosphere from room temperature up to 1000°C. The dehydration of the compounds takes place in one step and it points out that the six water molecules are bound in the same way. This assumption is confirmed by their IR spectra, where single sharp HOH deformation band at 1694 $cm^{-1}$ appears in both compounds.

The thermal decomposition of the anhydrous compounds starts at about 260°C and is very complex. This process takes place in many steps which are not well resolved.

The diisopropylammonium sulphate is prepared from the diisopropylamine by neutralization up to pH 3–4 with diluted sulphuric acid and permanent cooling in an ice-water bath.

**Keywords:** aluminium, chromium, double sulphates with diisopropylammonium, identification, sythesis, thermal decomposition

## Introduction

Double sulphates of *M*(III) with monovalent cations are subjects of many investigations. So, double sulphates of trivalent aluminium, chromium and iron 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 sulphates of the 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]. Beside the existence of iron alum with monomethylammonium it

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was found that other two compounds with 3.5 and 6 molecules of crystal water [8] also exist. 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-, tetramethyl-, diethyl-, ethanol-, diethanol-, and triethanolammonium cations [8–12]. The crystal structure of double sulphate of trivalent Al with dimethylammonium is determined and dimorphism of this compound is established [13]. Recently, the results of recorded FTIR and polarized Raman spectra of dimethylammonium aluminium sulphate hexahydrate have been presented [14, 15].

As a continuation of our work on double sulphates 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 sulphates of Al(III) and Cr(III) with diisopropylammonium(I) with general empirical formula: $M(CH_3CHCH_3)_2NH_2(SO_4)_2\cdot 6H_2O$ for which we have found no data in literature. An attempt was made to obtain a double sulphate with iron(III) with the same monovalent cation but without success.

## Experimental

### *Chemicals*

Diisopropylamine (purum), analytical grade aluminium for the preparation of aluminium sulphate solution ($c$= 0.5 mol dm$^{-3}$), analytical grade chromium(III) sulphate nonadecahydrate for the preparation of the solution ($c$= 0.5 mol dm$^{-3}$) and sulphuric acid (p.a., Merck).

### *Procedure for synthesis*

Double sulphates of Al(III) and Cr(III) with diisopropylammonium are obtained by evaporation at ambient temperature of a concentrated aqueous solution of *M*(III) sulphate (0.004 mole) and diisopropylammonium sulphate in a molar ratio 1:6 in the presence of 0.008 mole of sulphuric acid. The obtained crystalline products were filtered off, washed with ethanol, dried in air and characterized by elemental analyses, IR and X-ray powder diffraction patterns. The thermal behavior of the products was also investigated in temperature interval from ambient temperature up to about 1000°C.

Diisopropylammonium sulphate aqueous solution was obtained by neutralization of diisopropylamine with dilute sulphuric acid (1:1) to pH 3–4 with constant external cooling in an ice-water bath.

### *Analytical methods*

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

X-ray powder diffraction patterns were made on a Philips PW 1050 vertical goiometer with proportional counter, using graphite-monochromatized $\text{CuK}_\alpha$ radiation.

The FTIR spectra of the title complexes were recorded from KBr pellets with System 2000 interferometer (Perkin Elmer) in a P/N 21525 (Graseby Specac) variable-temperature cell with KBr windows.

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 $\text{min}^{-1}$ 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

The infrared spectra of the title compounds (Fig. 1) are practically identical, indicating possible isomorphism between the complexes. The spectra are dominated by the strong and broad absorption in the 3700–2100 $\text{cm}^{-1}$ interval with a maximum at 3029 $\text{cm}^{-1}$ corresponding to the ν(SO) mode. The upper frequency limit of the ν(OH/NH) absorption reveals that weakly hydrogen-bonded water molecules are also present in the respective structure. The appearance of a singlet sharp HOH deformation band (1624 $\text{cm}^{-1}$) might be an indication that the water molecules are structurally the same. On the other hand, the presence of two bands with shoulders from the lower-frequency side and alike appearance at 1477 and 1394 $\text{cm}^{-1}$ (the first of which is probably a doublet) in the HNH bending region (1500–1380 $\text{cm}^{-1}$) show that there are at least two crystallographic types of diisopropylammonium cations. The symmetric appearance of the ν(SO) band (1041 $\text{cm}^{-1}$), moreover, is probably due to the existence of $\text{SO}_4^{2-}$ ions with symmetry close to Td. The greater spectral difference in the external ammonium modes around 530 $\text{cm}^{-1}$ between the two salts is probably in connection with slightly different structural environment of the diisopropylammonium cations in the respective structures.

The X-ray powder diffraction patterns (Fig. 2) as well as IR-spectra confirmed that the investigated double sulphates are isostructural but different with respect to the crystal structure of aluminium and chromium dimethylammonium sulphate hexahydrates [9]. The isostructurality of Al and Cr double salts are confirmed in many cases [1, 2]. It is obvious from Fig. 2 that *d*-values of Cr-compound are higher than the corresponding *d*-values of Al-compound because of a larger ionic radius of Cr *vs*. Al. It is already well known that the stoichiometry of the double sulfates as well as their crystal structure depends on the ionic radii of both cations [16] as well as on the conditions of their synthesis [17].

From the results of the elemental analysis as well as from the mass of water and residue, determined by TG analysis, the following general formula could be supposed $\text{M(III)(CH}_3\text{CHCH}_3)_2\text{NH}_2(\text{SO}_4)_4\cdot 6\text{H}_2\text{O}$ ($M$=Al or Cr). In addition, the chemical formula suggests that – as in other double sulphates crystallohydrates – only six water molecules are probably coordinated with Al(III) and Cr(III) [1, 2, 13].

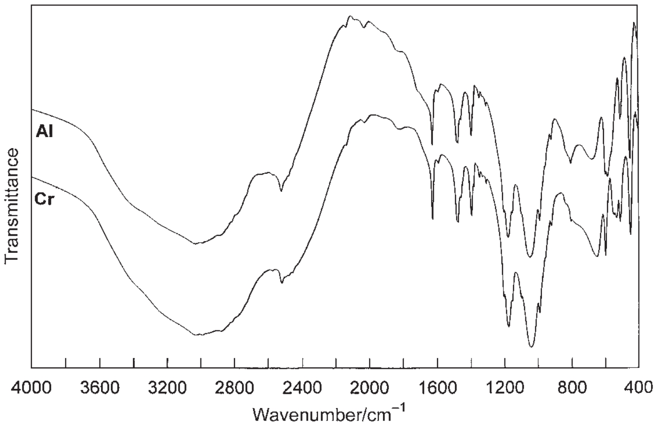

**Fig. 1** IR spectra of $M(CH_3CHCH_3)_2NH_2(SO_4)_2 \cdot 6H_2O$

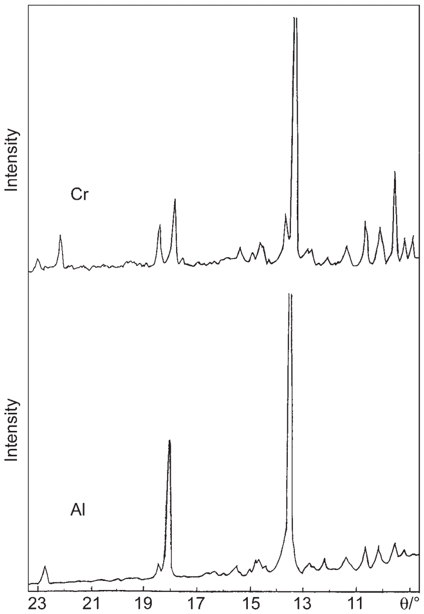

**Fig. 2** X-ray powder diffraction patterns of $M(CH_3CHCH_3)_2NH_2(SO_4)_2 \cdot 6H_2O$

# Thermal studies

The TG, DTG and DTA curves of the thermal decomposition of aluminium- and chromium diisopropylammonium sulphate hexahydrates are presented in Figs 3 and 4. Their thermal decomposition takes place in three stages. The first stage which

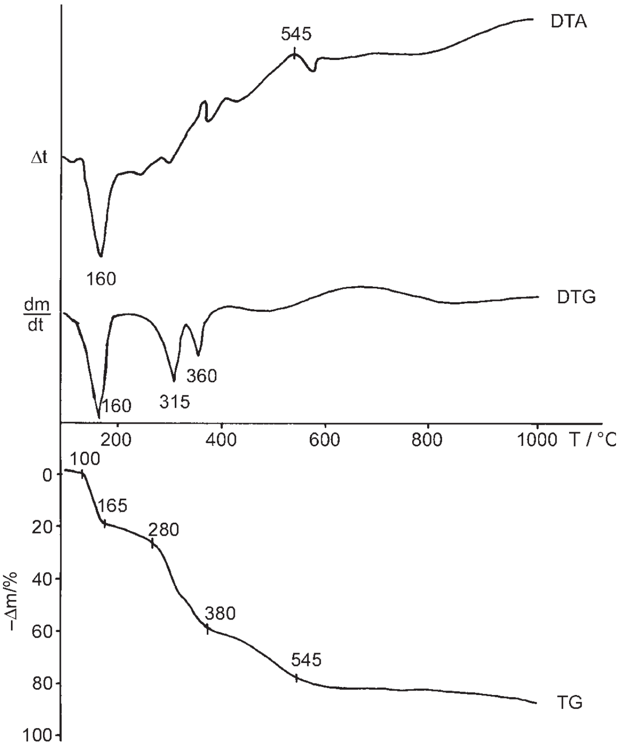

**Fig. 3** TG. DTG and DTA curves of $Al(CH_3CHCH_3)_2NH_2(SO_4)_2 \cdot 6H_2O$

is related with the dehydration of the compounds takes place in a similar temperature interval and in one step (DTG maximums at 140°C for Cr- and 160°C for Al compound), which indicates that six molecules of water are structurally the same. This stage is well resolved (with a horizontal level) from the next stage.

The second and the third stage are not well resolved and are differentiated only on the basis of the inflection points. In the second stage, the release of diisopropylammonium sulfate takes place in both compounds in a different way. In the aluminium compound (Fig. 3) it takes place in two steps (two DTG peaks at 315 and 360°C) whereas in chromium compound (Fig. 4) only in one step (one DTG peak at 305°C). On DTA curves only few weak peaks could be observed. In the third stage, the decomposition of metal(III) sulphate takes place. In this stage, the difference in the thermal decomposition of aluminium and chromium sulphate is obvious. The decomposition of chromium sulphate takes place in two well resolved steps and is connected with a strong exothermic peak at 495°C, whereas aluminium sulphate decomposes in one step and is connected with a weak exothermic peak at 545°C. The second and third stages take place in a similar temperature interval. Corresponding $M_2O_3$ as final product is obtained. The thermal decomposition could be presented with the following equations:

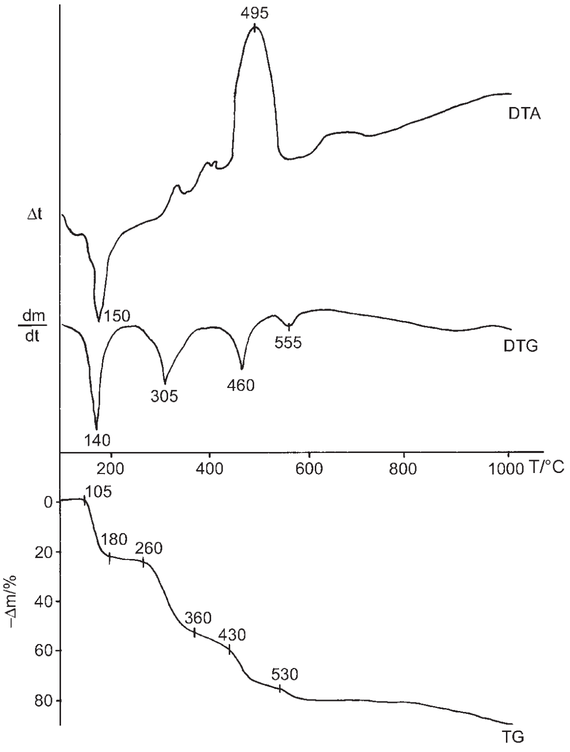

**Fig. 4** TG, DTG and DTA curves of $Cr(CH_3CHCH_3)_2NH_2(SO_4)_2{\cdot}6H_2O$

*I stage, from 100–165°C (Al) and 105–180°C (Cr)*

$M(CH_3CHCH_3)_2NH_2(SO_4)_2{\cdot}6H_2O \rightarrow M(CH_3CHCH_3)_2NH_2(SO_4)_2 + 6H_2O$
Mass loss: found (Al) 25.0% and (Cr) 24.0%; calculated 25.17 and 23.79% respectively.

*II stage (Al compound), from 270–380°C*

1st step: $2Al(CH_3CHCH_3)_2NH_2(SO_4)_2 \rightarrow 2(CH_3CHCH_3)_2NH + Al_2(SO_4)_3{\cdot}H_2SO_4$
Mass loss: found 23.0%; calculated 23.56%
2nd step: $Al_2(SO_4)_3{\cdot}H_2SO_4 \rightarrow SO_3 + H_2O + Al_2(SO_4)_3$
Mass loss: found 11.0%, calculated 11.41%

*II stage (Cr compound), from 260–420°C*

$2Cr(CH_3CHCH_3)_2NH_2(SO_4)_2 \rightarrow [(CH_3CHCH_3)_2NH_2]_2SO_4 + Cr_2(SO_4)_3$
Mass loss: found 34.0%, calculated 33.05%

*III stage (Al compound), from 380–600°C*

$Al_2(SO_4)_3 \rightarrow 3SO_3 + Al_2O_3$
Mass loss: found 29.0%, calculated 27.98%

*III stage (Cr compound), from 420–530–1000°C*

1st step: $Cr_2(SO_4)_3 \rightarrow Cr_2O_2SO_4$
Mass loss: found 18%, calculated 17.63%
2nd step: $Cr_2O_2SO_4 \rightarrow Cr_2O_3 + SO_3$
Mass loss: found 12%, calculated 8.8%

## Conclusions

- Double sulphates of Al and Cr with diisopropylammonium were obtained as crystallohydrates.
- Under the same conditions Fe(III) did not yield a solid double sulphate.
- The attempt to obtain double sulphate with *M*(II) as Cu, Ni, Co, Mn, Zn and Cd failed and only starting compounds were obtained.
- The obtained *M*(III) double sulphates hexahydrates are isostructural.
- They dehydrate above 100°C but anhydrous salts decompose beginning at about 250°C.

## References

1 B. H. Srezhkin, Koord. Khim., 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. Stepple, 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 D. 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 N. Galesic and V. B. Jordanovska, Acta Cryst., C48 (1992) 256.
14 V. P. M. Pillai, V. U. Nayar and V. B. Jordanovska, Optics and Optoelectronic, 1 (1998) 193.
15 V. P. M. Pillai, V. U. Nayer and V. B. Jordanovska, Spectrochim. Acta, 56A (2000) 887.
16 V. Petrusevski and S. Aleksovska, Croat. Chim. Acta, 64 (1991) 577.
17 L. N. Komissarova, Soedineniya redkozemel'nyh elementov. Sulfatiy, selenatiy, telluratiy, khromatiy, Nauka, Moskow 1986.