SYNTHESIS AND THERMAL DECOMPOSITION OF DOUBLE DIMETHYLAMMONIUM SULPHATE HEXAHYDRATES OF ALUMINIUM AND CHROMIUM

V. B. Jordanovska

INSTITUTE OF CHEMISTRY, UNIVERSITY "KIRIL AND METODIJ", 91000 SKOPJE, YUGOSLAVIA

Double sulphates of trivalent aluminium and chromium with dimethylammonium, with general formula $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$, were synthesized and studied by means of thermogravimetry and differential thermal analysis over the range 20–600 °C under dynamic conditions in a flow of dry nitrogen or air, and with the methods of chemical analysis. An X-ray powder diffraction study of the above compound was also undertaken. It is assumed that dimethylammonium aluminium sulphate hexahydrate and dimethylammonium chromium sulphate hexahydrate are isostructural. The mechanism of thermal decomposition of these double salts is also suggested.

The double sulphates of a monovalent alkalimetal or ammonium and a trivalent metal, with general formula $A^I B^{III}(SO_4)_2 \cdot 12H_2O$, are named alums. The physical and chemical properties of alums where B^{III} is aluminium or chromium and A^I is ammonium or monomethylammonium have been investigated by Boljšakova et al. [1]. The structure of alums has been a subject of investigation by many authors [2–11]. It was found that these compounds exist in three different types of cubic crystal (Pa3 space group), as α-, β- and γ-alums. It is evident from these previous studies that double sulphates with a given monovalent cation are usually isomorphosus.

The thermal behaviour and thermal decomposition of alums have also been reported [12–17]. Recently, we investigated the crystal structure [18] and the thermal decomposition [19] of dimethylammonium rare earth(III) sulphate tetrahydrates, and the difference in the thermal decompositions [20] of methylammonium rare earth(III) sulphate hydrates in air and in argon.

By analogy with the obtained alums of aluminium and chromium with monomethylammonium, it was expected that alums should also be obtained with dimethylammonium. This paper reports the synthesis and the chemical and thermal analysis data, together with X-ray powder diffraction patterns on double sulphates of aluminium and chromium with dimethylammonium.

Experimental

Materials and methods

Analytical grade metal was used for the preparation of aluminium sulphate solution. $C = 0.5$ mol $Al_2(SO_4)_3$ dm^{-3}, by dissolving aluminium foil in dilute sulphuric acid at pH 2. Chromium sulphate solution, $C = 0.5$ mol $Cr_2(SO_4)_3$ dm^{-1}, was prepared from analytical grade $Cr_2(SO_4)_3 \cdot 19H_2O$ and dilute sulphuric acid at pH 2. Dimethylammonium sulphate, $C = 0.69$ mol $[(CH_3)_2NH_2]_2SO_4$ dm^{-3} approximately, was prepared as described by Jordanovska and Siftar [21].

Double sulphates of aluminium and chromium with dimethylammonium were obtained as crystalline precipitates by isothermal evaporation of concentrated aqueous mixed solutions of metal(III) sulphates and dimethylammonium sulphate in the molar ratio 1 : 5, at room temperature. The crystals obtained were filtered off, washed with ethanol and dried at room temperature.

The thermoanalytical curves of the aluminium double sulphate were obtained with a Mettler thermoanalyser in dynamic dry air: flow velocity 5 l/h, Pt/Pt–Rh thermocouple, Pt crucibles (TD1), sample mass approximately 56 mg, heating rate 6 deg/min; and of both aluminium and chromium double sulphates using a Netzsch thermoanalyser M STA 429 in dynamic dry nitrogen, Pt/Pt–Rh thermocouple, quartz crucibles, sample mass approximately 30 mg, heating rate 2 deg/min. The reference for DTA determination was α-Al_2O_3. The temperature range was from 20 to 600°. The content of aluminium in the aluminium double sulphate was determined complexometrically with a standard solution of titriplex III (ethylene-dinitrilotetraacetic acid disodium salt dihydrate) with xylenol orange as indicator [21].

The chromium content in its double sulphate was not determined. For determination of the empirical formula of this double salt, analytical results for other elements and the identical powder diffraction pattern with that of the aluminium double salt were taken into consideration. Carbon, hydrogen and nitrogen were determined by means of elemental microanalysis. The densities of the double sulphates were measured with a pycnometer. The contents of crystal water were estimated from the TG diagrams via the mass losses in the dehydration processes.

The X-ray powder diffraction patterns were obtained with a JEOL X-ray diffractometer M MDX, goniometer M DX–GO–F, and Cu–K$_\alpha$ radiation, Ni-filtered.

Results and discussion

Thermoanalytical curves are shown in Figs 1 and 2. The results of quantitative chemical analysis are given in Table 1, and the experimental and calculated mass losses in Table 2. The general formula of the obtained double sulphates is $(CH_3)_2NH_2M^{III}(SO_4)_2 \cdot 6H_2O$.
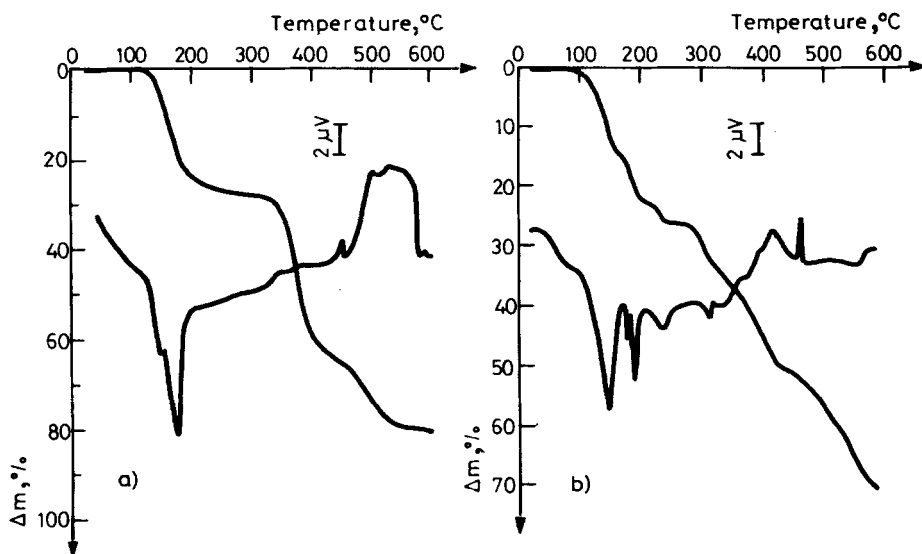
Fig. 1 TG and DTA curves of $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$
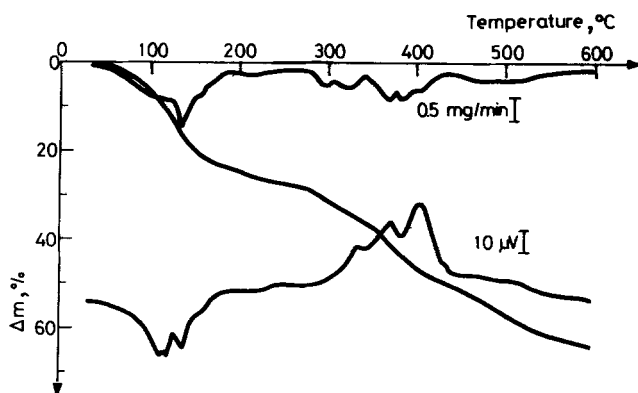
Fig. 2 TG, DTA and DTG curves of $(CH_3)_2NH_2Al(SO_4)_2 \cdot 6H_2O$

Table 1 Chemical analysis and density determinations of double sulphates $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$

M (molar mass)		C, %	H, %	N, %	M, %	ϱ, $g \cdot cm^{-3}$
Al (373.28 $g \cdot mol^{-1}$)	found	6.73	5.69	3.87	7.05	1.6215
	calcd.	6.43	5.40	3.75	7.23	
Cr (398.29 $g \cdot mol^{-1}$)	found	6.29	4.98	3.51		1.6414
	calcd.	6.03	5.06	3.42		

Table 2 TG mass losses of double sulphates $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$ in nitrogen

M (molar mass)		H_2O, %	$[(CH_3)_2NH_2]_2SO_4$, %	Total, %
Al (375.28 $g \cdot mol^{-1}$)	found	28.20	23.69	72.10
	calcd.	28.95	25.21	75.59
Cr (398.29 $g \cdot mol^{-1}$)	found	27.15	32.69	81.88
	calcd.	27.14	23.63*	80.97

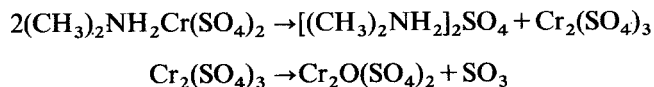* Calculated value if $Cr_2O(SO_4)_2$ is obtained: 33.83%.

The decompositions of the aluminium and chromium double sulphates in an atmosphere of dry nitrogen differ. In Fig. 1a, three clearly separated stages of thermal decomposition (TG curve) of dimethylammonium chromium sulphate hexahydrate are apparent. The first stage (from 80 to 260°) corresponds to dehydration. Two endothermic maxima (at 150 and 175°) in the DTA curve indicate gradual water loss. The second stage (from 270 to 410°) is associated with thermal decomposition of the anhydrous double sulphate to chromium(III) sulphate and subsequently to $Cr_2O(SO_4)_2$ (mass loss: found 32.69%, calcd. 33.83%). In the third stage, $Cr_2O(SO_4)_2$ decomposes to $Cr_2O_2SO_4$ in the first step (mass loss: found 10.39%, calcd. 10.20%) and to chromium(III) oxide in the second step (mass loss, total: found 81.88%, calcd. 80.97%). In general, the thermal decomposition of dimethylammonium chromium(III) sulphate hexahydrate can be written as:
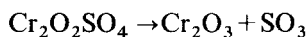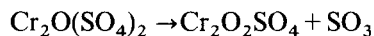
1st stage:

$$(CH_3)_2NH_2Cr(SO_4)_2 \cdot 6H_2O \rightarrow 6\,H_2O + (CH_3)_2NH_2Cr(SO_4)_2$$

2nd stage:

$$2(CH_3)_2NH_2Cr(SO_4)_2 \rightarrow [(CH_3)_2NH_2]_2SO_4 + Cr_2(SO_4)_3$$

$$Cr_2(SO_4)_3 \rightarrow Cr_2O(SO_4)_2 + SO_3$$

3rd stage:

$$Cr_2O(SO_4)_2 \rightarrow Cr_2O_2SO_4 + SO_3$$

$$Cr_2O_2SO_4 \rightarrow Cr_2O_3 + SO_3$$
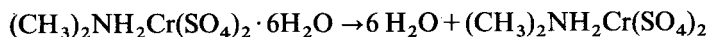
The X-ray diffraction pattern of the residual powder shows the presence of Cr_2O_3. This is in agreement with the earlier results on the thermal decomposition of ammonium chromium(III) sulphate dodecahydrate, where the $Cr_2(SO_4)_3$ obtained decomposed to Cr_2O_3 at 500–570° [14].

A sharp exothermic peak at 450° is probably due to oxidation of the separated carbon by SO_3:
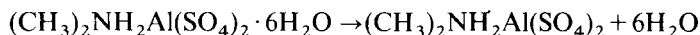
$$C + SO_3 = CO + SO_2$$
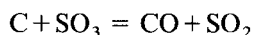
The thermal decomposition of the aluminium double sulphate in dry nitrogen (Fig. 1b) is more complicated than that of the chromium double sulphate. There are three stages of decomposition, with many steps involved. The dehydration process (first stage) from 70 to 270° proceeds in four steps and involves the gradual loss of water. In the second stage (from 280 to 410°), the anhydrous double sulphate decomposes to aluminium sulphate (mass loss: found 23.69%, calcd. 25.21%). In the third stage, aluminium sulphate decomposes to $Al_2O_2SO_4$ (total mass loss: found 72.10%, calcd. 75.59%). A sharp exothermic peak at 475° is probably due to oxidation of the separated carbon. The end-product at 600° is not clearly defined, because the X-ray diffraction pattern does not show any well-defined structure. From the mass loss calculation, it is suggested that $Al_2O_2SO_4$ is obtained.
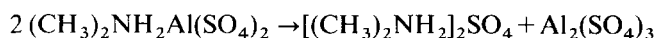
The thermal decomposition of the aluminium double sulphate in air (Fig. 2) also proceeds in three stages. The dehydration process is similar to that in nitrogen (mass loss: found 28.24% calcd. 28.95%), but in the second stage, decomposition of the anhydrous aluminium double sulphate proceeds with some exothermic effects (DTA curve) and aluminium sulphate is obtained (mass loss: found 23.8%, calcd. 25.21%). In the third stage, decomposition of aluminium sulphate to aluminium oxysulphate is suggested (total mass loss: found 63.39%, calcd. 64.91%). In general, the thermal decomposition of dimethylammonium aluminium sulphate hexahydrate can be written as:

in air

1st stage:

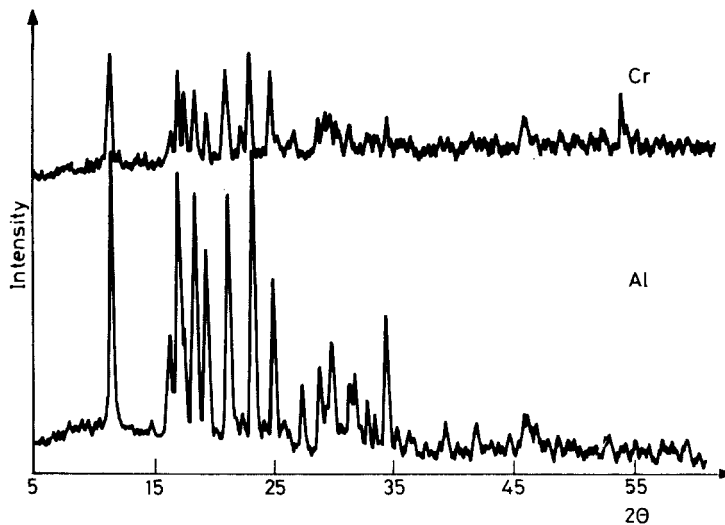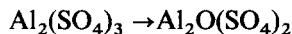$$(CH_3)_2NH_2Al(SO_4)_2 \cdot 6H_2O \rightarrow (CH_3)_2NH_2Al(SO_4)_2 + 6H_2O$$

2nd stage:

$$2 (CH_3)_2NH_2Al(SO_4)_2 \rightarrow [(CH_3)_2NH_2]_2SO_4 + Al_2(SO_4)_3$$

Fig. 3 X-ray powder diffraction patterns of $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$

3rd stage:

$$Al_2(SO_4)_3 \rightarrow Al_2O(SO_4)_2$$

in nitrogen, the 3rd stage is extended with:

$$Al_2O(SO_4)_2 \rightarrow Al_2O_2SO_4 + SO_3$$

The X-ray powder diffraction patterns (Fig. 3) of the crystal products show that the obtained double sulphates do not belong among the well-known alums of aluminium and chrlmium [22], and that the two compounds have identical structures.

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Zusammenfassung — Verbindungen der Formel $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$ mit M = Al(III) oder Cr(III) wurden synthetisiert und mittels TG und DTA im Intervall 20–600 °C unter dynamischen Bedingungen in bewegtem trockenen Stickstoff- oder Luftstrom sowie mittels chemischer Analyse untersucht. Auf Grund einer ebenfalls durchgeführten röntgenografischen Pulvermethode wurde festgestellt, daß Dimethylammonium-aluminiumsulfat-hexahydrat sowie Dimethylammonium-chromsulfat-hexahydrat isostrukturell sind. Ein Mechanismus für die thermische Zersetzung dieser Doppelsalze wird ebenfalls vorgeschlagen.

Резюме — Синтезированные двойные соли сульфатов алюминия и хрома с диметиламмонием общей формулы $(CH_3)_2NH_2M(SO_4)_2 \cdot 6H_2O$, были изучены методами химического анализа и методами ТГ и ДТА в температурном интервале 20–600° в динамических условиях в потоке сухого азота и воздуха. На основе порошкового рентгеноструктурного анализа были предположено, что гексагидраты солей обоих металлов являются изоструктурными. Предложен механизм термического разложения этих двойных солей.