Journal of Thermal Analysis, Vol. 38 (1992) 1563-1570

SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF DOUBLE MONOMETHYLAMMONIUM SULFATES OF COBALT, NICKEL, COPPER AND ZINC

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(Received March 3, 1991)

Double sulfates of cobalt(II), nickel(II), copper(II) and zinc with the monomethylammonium cation were obtained from the reaction mixture of the corresponding metal sulfate and monomethylammonium sulfate in a molar ratio of 1:3.

The obtained compounds were studied by the methods of X-ray powder diffraction, TG and DSC analysis and elemental analysis.

It was found that the double sulfates have the formula $(CH_3NH_3)_2M(SO_4)_2 \cdot 6H_2O$, and that the cobalt, nickel and zinc compounds are isostructural. The relationship between crystal structure and thermal decomposition is discussed.

Keywords: double sulphates

Introduction

Recently, great interest has been shown in double sulfates with nonmetallic cations. There are some data on the double sulfates of trivalent metal cations with monovalent aliphatic ammonium cations. Thus, the crystal structures of monomethylammonium alums of Al and Cr(III) [1–3] and a number of their physical and chemical properties are already known [4, 5]. Also, the double sulfates of aluminium and chromium with the dimethylammonium cation have been synthesized and their thermal decompositions studied [6]. Double sulfates of

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some lanthanides with the methylammonium or dimethylammonium cation have likewise been synthesized and studied [7–9].

So far, there are few data on the double sulfates of divalent metal cations with monovalent organic cations. Investigations have been made on the double sulfates of the divalent transition metals with the hydrazinium cation [10]. Recently, we reported on the synthesis and some investigations of the double sulfates of manganese and cadmium with the monomethylammonium cation [11].

Continuing our work on double sulfates of divalent and trivalent metal cations with monovalent organic cations, in this paper we present results relating to the synthesis and investigation of double sulfates of cobalt, nickel, copper and zinc with the monomethylammonium cation.

Experimental

Procedure

Double sulfates of cobalt, nickel, copper and zinc with the monomethylammonium cation were obtained by evaporation of the aqueous reaction mixture of the corresponding metal sulfate and monomethylammonium sulfate, at room temperature, in a molar ratio of 1:3. The crystal products were filtered off, washed with ethanol and dried in air.

The obtained compounds were characterized and investigated by X-ray powder diffraction, TG and DSC analysis, and elemental analysis.

Apparatus and methods

The X-ray diffraction patterns were obtained on a JEOL diffractometer, model JDX–7E, with CuK_α radiation, Ni-filtered with a goniometer, model DX–GO–F. The *d* values were corrected for the experimental error with α–SiO_2.

TG and DSC curves were obtained with a Mettler thermoanalyser in a flow of dry air. Experimental conditions: reference substance for DSC determination α–Al_2O_3, TG macrosample holder with Pt crucibles, heating rate 4 deg/min, temperature range 293–873 K.

A complexometric method was used for quantitative determination of the metal.

Results and discussion

The results of the quantitative chemical analysis (C, H, N and M(II) analysis and the mass losses, followed by the calculated values) are given in Table 1. The

results show that the obtained double sulfates have the empirical formula $(CH_3NH_3)_2M(SO_4)_2 \cdot 6H_2O$ (where $M = Co^{2+}$, Ni^{2+}, Cu^{2+} and Zn^{2+}).

Table 1 The results of the chemical and TG analysis of $(CH_3NH_3)_2M(SO_4)_2 \cdot 6H_2O$

	Co		Ni		Cu		Zn	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$\%M^{2+}$	13.92	13.76	13.88	13.48	14.85	14.46	15.21	15.31
%C	5.67	5.96	5.68	6.02	5.61	6.32	5.59	5.99
%H	5.71	6.03	5.72	6.46	5.65	5.51	5.62	5.90
%N	6.62	6.78	6.62	7.00	6.55	7.15	6.52	6.78
$\%H_2O$	25.54	24.17	25.55	23.05	25.26	24.29	25.15	23.56
$\%R_2SO_4$	37.84	37.14	37.86	39.40	37.44	37.10	37.28	37.02
$\%MSO_4$	36.62	37.44	36.58	37.55	37.29	38.29	37.52	38.94

The X-ray powder diffraction data (Fig. 1) show that the obtained compounds have a structure different from that of the well-known series of isomorphous double sulfates with general formula $M^{I}M^{II}(SO_4)_2 \cdot 6H_2O$, named Tuton's salts. The *d* values and the relative intensities of the obtained double sulfates are given in Table 2. From Fig. 1 and Table 2, it can be concluded that the double sulfates of cobalt, nickel and zinc are isostructural, but the copper compound has a different structure. All these results are in agreement with the crystal structure determination, which shows that the corresponding polyhedron around the copper is an elongated octahedron instead of the regular octahedron around cobalt [12]. The cobalt atom is surrounded by four water molecules and by two O atoms from the two SO_4 groups in the form of an almost regular octahedron. In the copper compound, the Cu atom is surrounded by four water molecules, but the two O atoms from the two sulfate groups are at longer Cu–O distances than the Cu–O_w distances. Both compounds crystallize in the triclinic PĪ group, with $Z=1$, in contrast with the Tuton's salts, which crystallize in the monoclinic $P2_1/\alpha$ space group with $Z=2$, where the metal is surrounded by six water molecules in a regular octahedron [13].

With the aim of finding relationships between the crystal structure and the thermal behavior, TG and DSC curves were recorded. The TG and DSC curves (Fig. 1) are similar for all the compounds, indicating in general two stages of thermal decomposition in the temperature range 293–873 K. In the first stage dehydration occurs, and in the second stage of thermal decomposition the anhydrous double sulfate decomposes. The final product of thermal decomposition up to 873 K was the corresponding metal sulfate in all cases, as concluded from the X-ray powder diffraction patterns of the residues [14], and also from the calculated and experimentally found values.

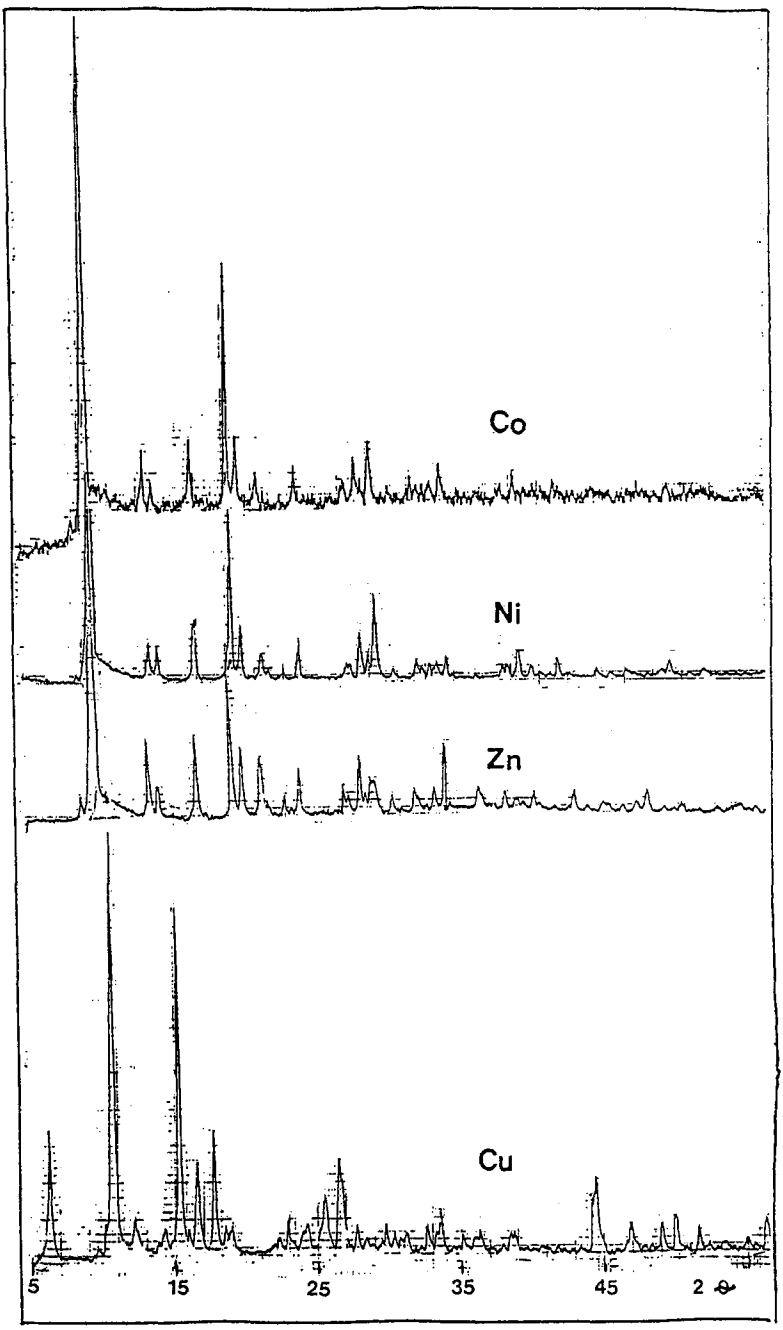

Fig. 1 The X-ray powder diffraction patterns of $(CH_3NH_3)_2M(SO_4)_2 \cdot 6H_2O$

Table 2 The *d*–values and relative intensities of $(CH_3NH_3)_2M(SO_4)_2{\cdot}6H_2O$

Co		Ni		Zn		Cu	
d / pm	I/I_o	*d* / pm	I/I_o	*d* / pm	I/I_o	*d* / pm	I/I_o
950.10	100	920.53	100	940.01	100	940.12	34
655.32	28	645.80	16	665.13	28	833.87	100
632.03	23	623.17	15	632.03	15	724.84	17
527.27	29	527.27	22	533.58	29	582.39	82
461.87	59	459.50	55	466.69	45	536.79	28
443.57	31	443.57	21	445.77	26	500.65	35
414.86	25	412.95	13	420.69	22	345.01	21
370.47	25	368.96	17	372.00	20	336.06	28
316.17	26	315.08	18	317.27	23	267.27	17
305.57	35	303.54	30	306.60	17	203.85	26

Although the thermal decompositions are similar, there are some differences in each case. Therefore, the thermal decomposition should be discussed for each compound.

The thermal decomposition of the Co complex takes place in several steps. In the first step of decomposition the compound loses four water molecules, in the temperature range 313–353 K (calc. value 17.02%, found 17.53%), followed by an endothermic peak at 335 K. This peak is connected with dissolution of the compound in the crystal water on loss of a part of the water. In the second step of decomposition, in the temperature range 383–423 K, the compound loses 1.5 water molecules, which is followed by an endothermic peak at 392 K (calc. value 6.39%, found 6.16%).

The hemihydrate is stable up to 483 K. In the third step of decomposition the compound loses the remaining 0.5 water molecules, and in the same stage decomposition of the anhydrous salt occurs. Thus in the temperature range 483–588 K, the compound loses 0.5 water molecules and H_2SO_4, which is followed by an endothermic peak at 578 K (calc. value for 0.5 H_2O and H_2SO_4 25.18%, found 26.54%). In this case, $CoSO_4{\cdot}2CH_3NH_2$ appears as an intermediate which exists in a short temperature interval. It decomposes to $CoSO_4$ in the temperature range 593–673 K (calc. value for $2CH_3NH_2$ 14.65%, found 11.85%), which is followed by two endothermic peaks at 608 K and 653 K. The experimental value for the residue ($CoSO_4$) is somewhat greater, which is probably due to the C remaining from methylamine decomposition [15] (calc. value for $CoSO_4$ 36.62 %, found 37.92 %).

The thermal decomposition for the Co compound can be expressed as:

$$(CH_3NH_3)_2Co(SO_4)_2{\cdot}6H_2O \xrightarrow{-4H_2O} (CH_3NH_3)_2Co(SO_4)_2{\cdot}2H_2O$$

$$\xrightarrow[-1.5\,H_2O]{} (CH_3NH_3)_2Co(SO_4)_2{\cdot}0.5H_2O \xrightarrow[-(0.5\,H_2O,\ H_2SO_4)]{}$$

$$CoSO_4{\cdot}2CH_3NH_2 \xrightarrow[-2\,CH_3NH_2]{} CoSO_4$$

The thermal decomposition of the nickel compound is very similar to that of the cobalt compound. In the temperature range 313–483 K, the compound loses 5.5 water molecules (calc. value 23.24%, found 23.05 %) in two steps, which are not so clearly separated as in the case of the Co compound. In the DSC curve, there are two endothermic peaks at 343 and 403 K, connected wit dehydration, and the former also with dissolution of the compound in the crystal water. In the temperature range 493–693 K, loss of the remaining 0.5 water molecules and decomposition of the anhydrous double sulfate take place in two steps. In the first step, in the temperature range 493–603 K, the compound loses 0.5 water molecules and H_2SO_4 (theor. value for H_2SO_4 and 0.5 H_2O 25.47%, found 27.50%). Here similarly as for the Co compound, the intermediate $NiSO_4{\cdot}2CH_3NH_2$ is formed, which further decomposes to $NiSO_4$ in the temperature range 643–693 K (calc. value for $NiSO_4{\cdot}2CH_2NH_2$ 14.65 %, found 12.27%). This stage of decomposition is followed by endothermic peaks at 408 and 582 K.

The thermal decomposition of the Ni compound can be expressed as:

$$(CH_3NH_3)_2Ni(SO_4)_2{\cdot}6H_2O \xrightarrow[-5.5\,H_2O]{} (CH_3NH_3)_2Ni(SO_4)_2{\cdot}0.5H_2O$$

$$\xrightarrow[-(0.5\,H_2O,\ H_2SO_4)]{} NiSO_4{\cdot}2CH_3NH_2 \xrightarrow[-2\,CH_3NH_2]{} NiSO_4$$

The thermal decompositions of the zinc and copper compounds take place only in two stages, without clearly separated steps. In the first stage, dehydration occurs. The Cu compound loses its water in the temperature range 313–483 K (calc. value 25.26%, found 24.29%) and the Zn compound does so at 313–463 K (calc. value 25.15%, found 23.56%). The dehydration process is followed by two endothermic peaks (DSC curve) for both compounds. The DSC maxima for the Cu compound are at 331 and 413 K, and for the Zn compound at 326 and 421 K. The first peak in both cases is connected with dissolution of the compound in the crystal water and loss of the water.

In the second stage of thermal decomposition, the decomposition of the anhydrous double salt to metal(II) sulfate takes place in both cases. For the Cu compound it takes place at 487–673 K (calc. value for methylammonium sulfate 37.44%, found 37.1%), and for the Zn compound at 323–653 K (calc. value for methylammonium sulfate 37.28%, found 37.02%). The final product of thermal decomposition at 873 K is the corresponding metal sulfate in both cases (calc. value for $CuSO_4$ 37.29%, found 38.59%; calc. value for $ZnSO_4$ 37.57%, found 38.94%). In the DTA curve for the Zn compound there are endothermic peaks at

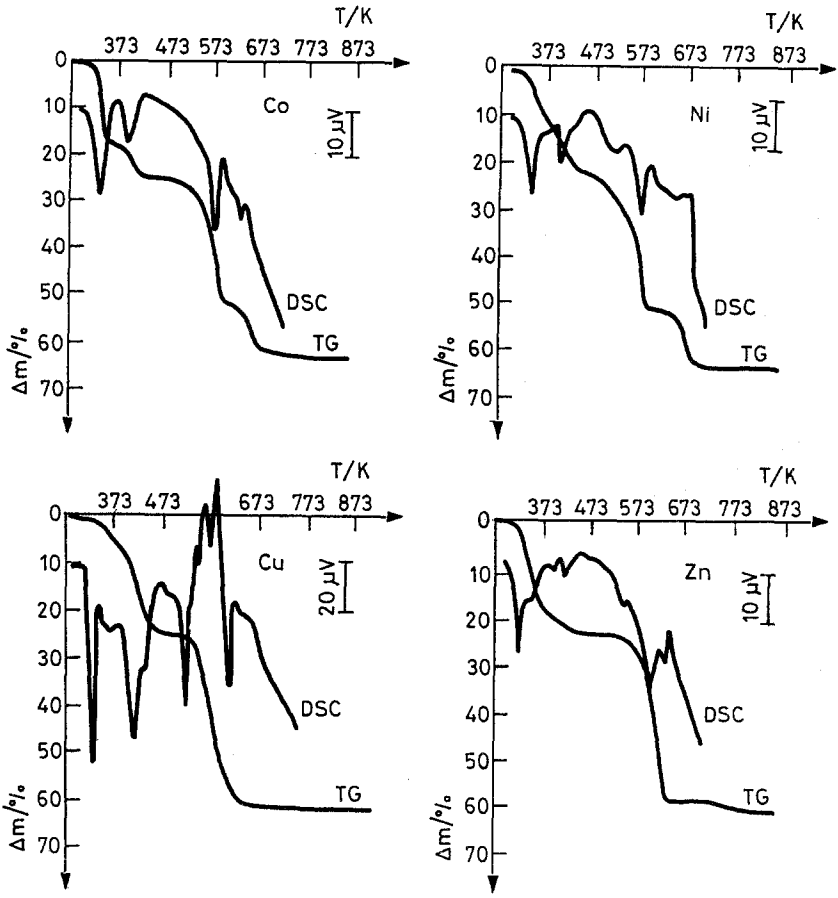

Fig. 2 TG and DSC curves of$(CH_3NH_3)_2M(SO_4)_2{\cdot}6H_2O$

608 and 633 K, and in that for the Cu compound there are two endothermic peaks at 323 and 620 K, but also an exothermic peak at 593 K.

The thermal decomposition for both compounds can be expressed as:

$$(CH_3NH_3)_2M(SO_4)_2{\cdot}6H_2O \xrightarrow{-6\,H_2O} (CH_3NH_3)_2M(SO_4)_2$$

$$\xrightarrow{-(CH_3NH_3)_2SO_4} MSO_4 \qquad (M{=}Cu, Zn)$$

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The financial support of the Research Council of Macedonia, Yugoslavia, is gratefully acknowledged.

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Zusammenfassung — Aus dem Reaktionsgemisch von Kobalt(II)-, Nickel(II)-, Kupfer(II)- und Zinksulfat mit Monomethylammoniumsulfat im Molverhältnis 1:3 werden die Doppelsulfate der entsprechenden Metalle mit dem Monomethylammoniumkation erhalten.
Die erhaltenen Verbindungen wurden mittels Röntgen-Pulverdiffraktion, TG, DSC und Elementaranalyse untersucht.
Es wurde festgestellt, daß die allgemeine Formel der Doppelsulfate $(CH_3NH_3)_2M(SO_4)_2{\cdot}6H_2O$ beträgt und daß es sich bei den Kobalt-, Nickel- und Zinkverbindungen um isostrukturelle Verbindungen handelt. Es wird die Beziehung zwischen Kristallstruktur und thermischer Zersetzung besprochen.