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SYNTHESIS AND INVESTIGATION OF DOUBLE SULFATES OF CADMIUM AND MANGANESE(II) WITH THE MONOMETHYLAMMONIUM CATION

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Double sulfates of Cd^{2+} and Mn^{2+} with monomethylammonium cation, were obtained by evaporation at room temperature, from an aqueous solution mixture of the corresponding metal sulfate, and monomethylammonium sulfate, in molar ratio 1:3.

The obtained crystals were investigated by the methods of X-ray powder diffraction, thermal analysis and elemental analysis.

The results of the thermal and elemental analyses indicate that the obtained double sulfates of cadmium and manganese are dihydrates, contrary to those of Co^{2}, Ni^{+2}, Cu^{+2} and Zn^{2+}, obtained in the same conditions, which are hexahydrates.

The X-ray powder diffraction patterns of the double monomethylammonium sulfates of Cd^{2+} and Mn^{2+} show that they are isostructural.

From the results of the thermal and elemental analysis, it can be concluded that the obtained compounds have the empirical formula $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$.

INTRODUCTION

There are many data about double sulfates of transition metals with a number of monovalent cations, but no data have been found about the double sulfates of divalent metal cation with the monomethylammonium cation. Also, some alums with monomethylammonium are known. The crystal structures of monomethylammonium alums of Al and Cr [1-3] and a number of their physical and chemical properties are already presented [4,5].

The synthesis and characterization of double sulfates of cobalt,

nickel copper and zinc with monomethylammonium cation [6], and the crystal structure have been recently presented [7]. Double sulfates of cobalt, nickel and zinc with dimethylammonium cation were synthesized and investigated too [8].

Continuing our work on double sulfates of divalent [6-8] and trivalent [9,10] metals with monovalent organic cations, in this paper we present the results of the preparation and characterization of double sulfates of cadmium and manganese(II) with the monomethylammonium cation.

EXPERIMENTAL PROCEDURE

Double sulfates with empirical formula $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$ (where M is Cd^{2+} or Mn^{2+}) were obtained from the reaction mixture of monomethilammonium sulfate and the corresponding metal sulfate aqueous solutions, in molar ratio 3:1. The mixture was evaporated at room temperature and treated with ethanol. The obtained crystals were filtered off, washed with ethanol and dried in air. The compounds were identified and studied by the methods of X-ray powder diffraction, TG and DSC-analysis, and elemental analysis.

APPARATUS AND METHODS

The X-ray powder diffractometer patterns were obtained on JEOL diffractimeter model JDX-7E, by Cu K_α-radiation, Ni filtered, with a goniometer model DX-GO-F.

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 makrosample Holder with Pt-crucibles, heating rate 4 °C/min, temperature range from 20-500 °C.

RESULTS AND DISCUSSION

The fact that double sulfates of cadmium and manganese(II) with the monomethylammonium cation are synthesized in the same manner as previously obtained double sulfates of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, which are hexahydrates [6], indicated that the compounds of the same type would be

expected. However, the results of the quantitative chemical analysis (C, H, N analysis, and complexometric determination of metals), and the calculated mass losses in the thermal decomposition (Table I), show that these compounds are not hexahydrates.

Table I. *The results of the elemental and TG-analysis of* $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$ $(M = Cd^{2+}, Mn^{2+})$

%	$(CH_3NH_3)_2Cd(SO_4)_2 \cdot 2H_2O$		$(CH_3NH_3)_2Mn(SO_4)_2 \cdot 2H_2O$	
	theor.	exper.	theor.	exper
C	5.94	5.47	6.92	7.63
H	3.98	4.14	4.64	4.31
N	6.92	5.83	8.07	8.93
M^{2+}	27.78	27.05	15.82	15.19
H_2O	8.90	9.39	10.38	8.61
MSO_4	51.51	53.53	43.49	42.59

The literature data [11] point out to the existence of double sulfates of cadmium an manganese(II) with K^+, obtained at 25°C which are dihydrates and at 40°C, with 1.5 water molecules. Our investigations show that the obtained compounds at room temperature are dihydrates, with empirical formula $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$ $(M = Cd^{2+}, Mn^{2+})$.

The X-ray powder diffraction patterns (Fig. 1) show that the double sulfates of cadmium and manganese(II) with monomethylammonium cation are isostructural. The d-values were corrected for the experimental error with αSiO_2. The d-values and relative intensities are given in Table II.

TG and DSC curves of the obtained compounds are shown on Fig. 2 (a, b).

The thermal decomposition of $(CH_3NH_3)_2Cd(SO_4)_2 \cdot 2H_2O$ takes place in two stages (Fig. 2a). In the first stage of decomposition, in the temperature range from 50-160 °C the compound loses the water which is followed by endothermic peak at 128 °C (calculated value 8.9%, found 9.39%). In the second stage, the decomposition of the anhydrous double sulfate occurs. This stage begins at 240 °C, and it takes place in two steps, followed by endothermic peaks at 328 °C and 409 °C (DSC curve). The final product of the thermal decomposition at 500 °C is $CdSO_4$. It was confirmed by the X-ray

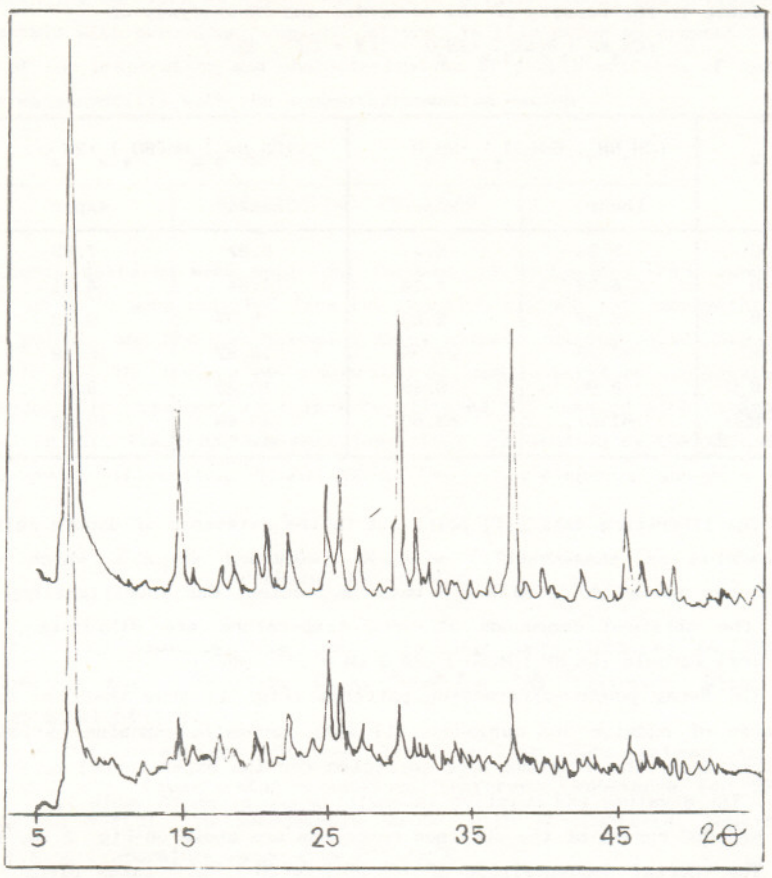

Fig. 1 X-ray powder diffraction patterns of $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$ (a: M =Cd, b: M = Mn)

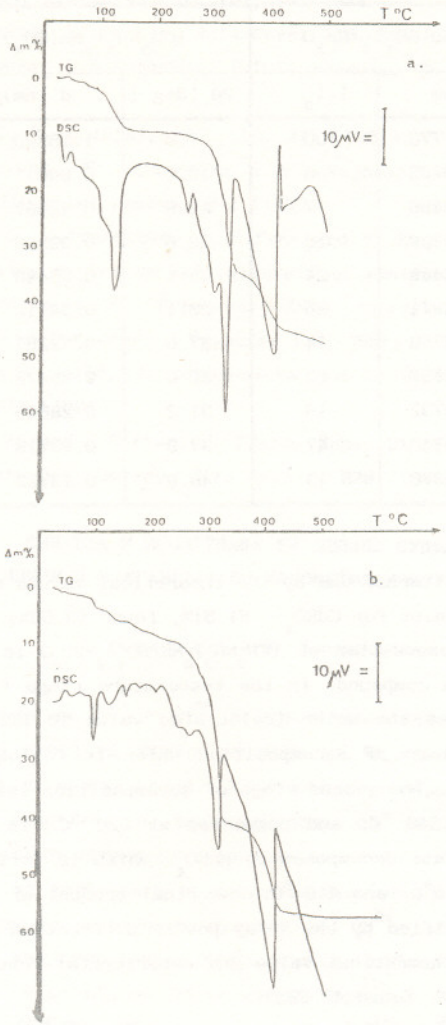

Fig. 2 *TG and DSC curves of* $(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O$
(a: M =Cd, b: M = Mn)

Table II. *The d-values and relative intensities of the obtained compounds*

$(CH_3NH_3)_2Cd(SO_4)_2 \cdot 2H_2O$			$(CH_3NH_3)_2Mn(SO_4)_2 \cdot 2H_2O$		
2θ (deg.)	d (nm	I/I_0	2θ (deg.)	d (nm)	I/I_0
7.5	1.17770	100	7.6	1.16220	100
14.9	0.59405	36	15.0	0.59011	26
20.4	0.43496	17	20.9	0.42467	23
22.6	0.39309	15	22.6	0.39303	26
25.1	0.35448	24	25.1	0.35448	39
15.9	0.34371	25	26.1	0.34112	32
27.2	0.32756	14	27.6	0.32291	25
29.9	0.29857	52	30.0	0.29472	27
31.1	0.28732	18	31.2	0.28643	22
37.7	0.23840	47	37.9	0.23719	30
45.6	0.19876	19	46.0	0.19723	22

powder diffraction patterns, and by the theoretical values and experimental results (calculated value for $CdSO_4$ - 51.51%, found 53.53%).

The thermal decomposition of $(CH_3NH_3)_2Mn(SO_4)_2 \cdot 2H_2O$ is similar to the isostructural cadmium compound. In the temperature range from 40°C to 220 °C, the compound loses the water (calculated value 10.38%, found 8.61%). This is the first stage of decomposition which is followed by an endothermic peak at 95 °C. The second stage of decomposition takes place in two steps. It begins at 240 °C, and completes at 420 °C. In this stage the anhydrous double sulfate decomposes to $MnSO_4$, which is followed by two endothermic peaks at 315°C, and 410 °C. The final product of the thermal decomposition was identified by the X-ray powder diffraction patterns of the residue, and by the theoretical value and experimental results (calculated value for $MnSO_4$ 43.49%, found 42.59%).

Generaly, the thermal decomposition to 500 °C of both compounds can be expressed as:

$$(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O \xrightarrow[-\,2H_2O]{\text{stage I}} (CH_3NH_3)_2M(SO_4)_2 \xrightarrow[-(CH_3NH_3)_2SO_4]{\text{stage II}} MSO_4$$

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СИНТЕЗА И ИСПИТУВАЊЕ НА ДВОЈНИ СУЛФАТИ НА КАДМИУМ И МАНГАН(II) СО МОНОМЕТИЛАМОНИУМ КАТЈОНОТ

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Двојни сулфати на Cd^{2+} и Mn^{2+} со монометиламониум катјонот добиени се со испарување на смеса од водени раствори на кадмиум сулфат и манган(II) сулфат соодветно, во молски однос 1:3, на собна температура.

Издвоените кристали се идентифицирани со методите на рендгенска дифракција на прашочни примероци, термичка анализа и елементарна анализа.

Резултатите од термичката и елементарната анализа покажуваат дека за разлика од претходно добиените сулфати на Co^{2+}, Ni^{2+}, Cu^{2+} и Zn^{2+} со монометиламониум катјонот кои се хексахидрати, добиените двојни сулфати на кадмиум и манган се дихидрати, со емпириска формула:

$$(CH_3NH_3)_2M(SO_4)_2 \cdot 2H_2O \qquad (M = Cd^{2+},\ Mn^{2+}).$$

Рендгенските прашочни дифрактограми покажуваат дека добиените двојни сулфати на кадмиум и манган се изоструктурни.

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