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Double sulfates of M(II) with ethanolammonium (where M is Mn, Co, Ni, Cu, Zn or Cd)

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Abstract

By evaporation of an aqueous mixture of metal(II) sulfate and ethanolammonium sulfate in the molar ratio 1:4 at room temperature, double sulfates with empirical formula $(HOCH_2CH_2NH_3)_2M(SO_4)_2 \cdot 4H_2O$ (where M is Mn, Co, Ni, Cu, Zn, or Cd) were obtained. The double salts obtained were identified by X-ray powder diffraction, elemental analysis, TGA, and DTA. The compounds have similar structures (the copper compound is an exception); the Mn, Co, Ni, and Zn compounds are isostructural. The manner of their thermal decomposition is also given.

INTRODUCTION

Double sulfates of M(II) with various monovalent cations have been the subject of many investigations. Tuton's salts with the empirical formula $M^I_2[M^{II}(H_2O)_6](SO_4)_2$ (where M^I is K, Rb, Cs, Tl(I), or NH_4^+; and M^{II} is Fe, Mn, Co, Ni, Cu, Zn, Mg, V, or Ru) are well known. They crystallize in the monoclinic P21/a space group with $Z = 2$ [1, 2] in which M(II) is coordinated with six molecules of water. Their thermal behavior has also been investigated [3–5]. Recently, the influence of M(II) on the thermal stability of Tuton's salts has been investigated. It was found that dehydration takes place at a lower temperature on decreasing the difference in the ionic radii of M(II) and M(I) [6]. Langfelderova et al. [7, 8] have investigated the dependence of the dehydration on the distortion of $[Cu(H_2O)_6]^{2+}$ in various Tuton's salts. It was found that in the case of rhombic distortion four molecules of water leave in the first step of the dehydration, but in the case of tetragonal distortion only two molecules, leave.

There are few data on the double sulfates of M(II) with nonclassical monovalent cations such as hydrazinium [9, 10] or on the thermal decomposition of Fe(II) with ethylenediammonium [11]. Recently we have

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presented data on the double sulfates of M(II) with methyl ammonium [12, 13] and dimethylammonium [14] cations.

Continuing our work on the double sulfates of M(II) with organic cations, we present in this paper results on the preparation and characterization of double sulfates of M(II) (where M is Mn, Co, Ni, Cu, Zn, or Cd) with the ethanolammonium cation, on which we have not found any data. The thermal behavior of these compounds has also been investigated.

EXPERIMENTAL

Procedures and methods

Double sulfates of M(II) with the ethanolammonium cation were obtained as crystaline products by evaporation at room temperature of an aqueous reaction mixture of M(II) sulfate (0.0035 mol) and ethanolammonium sulfate (pH 4–5) in the molar ratio 1:4. The aqueous solution of ethanolammonium sulfate (1.5 mol dm^{-3}) was prepared by stepwise neutralization of 2-ethanolamine (Merck, purum) with dilute sulfuric acid to pH 4–5. The color of the crystals of the double sulfates obtained was somewhat lighter than that of the starting M(II) sulfate. The crystaline products were filtered off, washed with ethanol and dried in a desiccator. The isolated double sulfates were examined using elemental analysis, X-ray powder diffraction, thermogravimetry (TG) and differential thermal analysis (DTA).

Elemental analyses of C and H by Liebig's method and the carbon–hydrogen analyzer Coleman Model 33, and of N by the Dumas method were carried out.

The X-ray powder diffraction patterns were obtained with a Philips PW 1050 vertical goniometer with a proportional counter, using graphite monochromatized Cu Kα radiation.

Thermogravimetric analyses were carried out on a recording Cahn RG Electrobalance in an air atmosphere at a heating rate of 5°C min^{-1}, from 20 up to about 900°C, using 10–13 mg of sample in a quartz crucible. Differential thermal analyses were made on the Netzsch differential thermal analyzer. The DTA curves were obtained in static air atmosphere, with samples varying in mass from 70 to 100 mg, at a heating rate of 5°C min^{-1} from ambient temperature to 900°C. The reference substance was pure alumina.

RESULTS AND DISCUSSION

From the X-ray powder diffraction patterns of the crystal products obtained it was found that new compounds with very similar structures (the copper compound is of a different structure) were obtained, and that the cobalt, nickel, manganese and zinc compounds are isostructural. Using

TABLE 1

Results of the elemental and thermal analysis of $(HOCH_2CH_2NH_3)_2M(SO_4)_2 \cdot 4H_2O$ [a]

M(II)	M_r	%H	%C	%N	$\%H_2O$	$\%M_xO_y$
Mn	443.31	5.84	11.77	7.01	16.40	16.32
		(5.46)	(10.84)	(6.32)	(16.25)	(Mn_2O_3, 17.81)
Co	447.30	5.23	11.06	6.00	16.47	15.96
		(5.40)	(10.74)	(6.26)	(16.11)	(Co_3O_4, 17.94)
Ni	447.08	5.26	10.84	6.64	16.77	15.63
		(5.41)	(10.75)	(6.27)	(16.12)	(NiO, 16.71)
Cu	451.90	5.79	11.20	5.87	14.63	17.32
		(5.35)	(10.63)	(6.20)	(15.94)	(CuO, 17.60)
Zn	453.74	5.27	11.30	6.14	16.20	14.46
		(5.33)	(10.59)	(6.17)	(15.88)	(ZnO, 17.93)
Cd	500.77	4.59	10.39	5.80	14.17	28.42
		(4.83)	(9.59)	(5.60)	(14.39)	(CdO, 25.64)

[a] Calculated values are given in parentheses.

elemental and thermal analysis it was also found (Table 1) that double sulfates with the empirical formula $(HOCH_2CH_2NH_3)_2M(SO_4)_2 \cdot 4H_2O$ (where M is Mn, Co, Ni, Cu, Zn, or Cd) were obtained. They do not have the structures of Tuton's salts, and are not hexahydrates but tetrahydrates such as $(CH_2NH_3)_2Fe(SO_4)_2 \cdot 4H_2O$ [11]. The fact that two different X-ray powder diffraction patterns were obtained for the copper compound from a sample which was first stored in a closed tube and then exposed to air for 11 days points to a structural change in the copper compound, whereas the other compounds are stable.

Because there is a difference in the thermal decomposition of the investigated compounds (Fig. 1), the thermal behavior of each compound is given separately.

M(II) is Mn ($M_r = 443.31$)

As can be seen from the Mn TG curve in Fig. 1, the thermal decomposition of the Mn compound takes place in three stages. In the first stage the dehydration of the compound takes place in two steps with three endothermic peaks. The first endothermic peak is somewhat larger than the others two, which means that in this step the compound melts and loses about one third of its crystal water. In the second stage (over a wide temperature interval), thermal decomposition of the anhydrous salt to $MnSO_4$ occurs. In the third stage, thermal decomposition of manganese sulfate to Mn_2O_3 take place. The X-ray powder diffraction pattern of the residue is consistent with a mixture of Mn_2O_3 (Powder Diffraction File No. 10-69 [15]) and γ-Mn_2O_3 (Powder Diffraction File No. 6-0540 [15]).

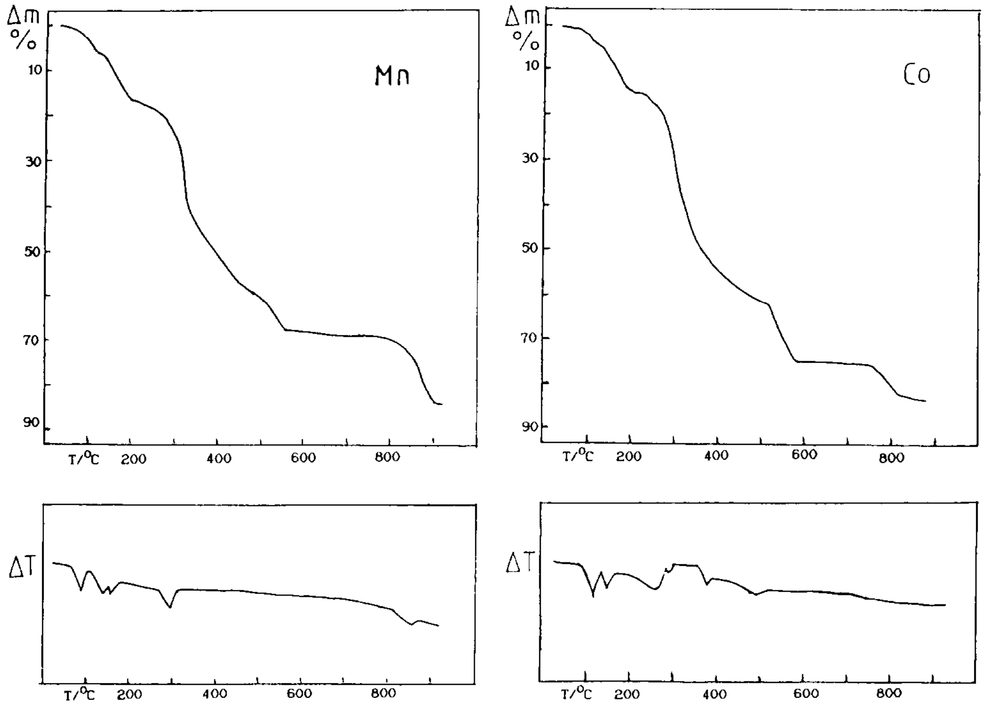

Fig. 1. TG and DTA curves of $(RH)_2M(SO_4)_2 \cdot 4H_2O$ (where M is Mn or Co).

Thermal decomposition can be expressed by the following equations ($RH = HOCH_2CH_2NH_3^+$; $R = HOCH_2CH_2NH_2$).

Stage 1 (42–219°C)

$(RH)_2Mn(SO_4)_2 \cdot 4H_2O \rightarrow 4H_2O + (RH)_2Mn(SO_4)_2$

Mass loss: found, 16.40%; calculated, 16.25%.

Stage 2 (219–558°C)

$(RH)_2Mn(SO_4)_2 \rightarrow (RH)_2SO_4 + MnSO_4$

Mass loss: found 51.21%; calculated, 49.68%.

Stage 3 (558–900°C)

$2MnSO_4 \rightarrow Mn_2O_3 + SO_2 + SO_3$

Mass loss: found, 16.07%; calculated, 16.26%. The mass of the residue is 16.32%; the calculated value for Mn_2O_3 is 17.81%.

M(II) is Co ($M_r = 447.30$)

As can be seen from the Co TG curve in Fig. 1, the thermal decomposition of the Co compound takes place in four stages. In the first stage, the crystal water leaves in two steps. On the DTA curve two endothermic peaks can be seen, the first of which is larger and corresponds to the smaller mass loss. This means that in this step the compound also melts (like the Mn compound). In the second stage the anhydrous double salt decomposes to ethanolammonium sulfate and cobalt(II) sulfate. In the third and fourth stages cobalt(II) sulfate decomposes stepwise to Co_3O_4. The X-ray diffraction pattern of the residue at about 900°C shows the presence of mainly Co_3O_4 (according to Power Diffraction File No. 4-418 [15]).

Stage 1 (34–242°C)

$(RH)_2Co(SO_4)_2 \cdot 4H_2O \rightarrow 4H_2O + (RH)_2Co(SO_4)_2$

Mass loss: found 16.47%; calculated, 16.11%.

Stage 2 (242–518°C)

$(RH)_2Co(SO_4)_2 \rightarrow CoSO_4 + (RH)_2SO_4$

Mass loss: found, 45.69; calculated, 49.24%.

Stages 3 and 4 (518–900°C)

In these two stage cobalt(II) sulfate decomposes and oxidizes to Co_3O_4. Mass loss: found, 22.21%; calculated, 16.71%.

M(II) is Ni ($M_r = 447.08$)

The compound loses its crystal water in the first stage of the thermal decomposition, in a similar way to the Co compound (Fig. 2, Ni TG curve). The compound also melts in the first step, as can be seen from the DTA curve. In the second stage, the thermal dissociation of the anhydrous double salt takes place and begins at a temperature higher than 220°C. In the third stage, the formation of a basic salt is suggested. As a final product, NiO is obtained, (according to Powder Diffraction File No. 4-835 [15]). On the basis of the mass losses, the following decomposition sequence is proposed.

Stage 1 (34–219°C)

$(RH)_2Ni(SO_4)_2 \cdot 4H_2O \rightarrow 4H_2O + (RH)_2Ni(SO_4)_2$

Mass loss: found, 16.77%; calculated, 16.12%.

Stage 2 (219–478°C)

$(RH)_2Ni(SO_4)_2 \rightarrow (RH)_2SO_4 + NiSO_4$

Mass loss: found, 48.55%; calculated, 49.26%.

Stage 3 (478–538°C)

$3NiSO_4 \rightarrow Ni_3O_2SO_4 + 2SO_3$

Mass loss: found, 13.95%; calculated, 11.94%.

Stage 4 (538–897°C)

$Ni_3O_2SO_4 \rightarrow 3NiO + SO_3$

Mass loss: found, 5.1%; calculated, 5.97%. The mass of the residue is 15.63%; the calculated value for NiO is 16.71%.

M(II) is Zn ($M_r = 453.74$)

Thermal decompositon of the Zn compound (Fig. 2, Zn TG curve) takes place in only three stages. In the first stage, the compound loses four water molecules followed by two endothermic peaks. In the second stage, the anhydrous double salt loses one molecule each of ethanolamine and sulfuric acid, and a monoamine complex is obtained.

From the X-ray powder diffraction pattern of the residue it is concluded that ZnO is obtained (Powder Diffraction File No. 36-1451 [15]).

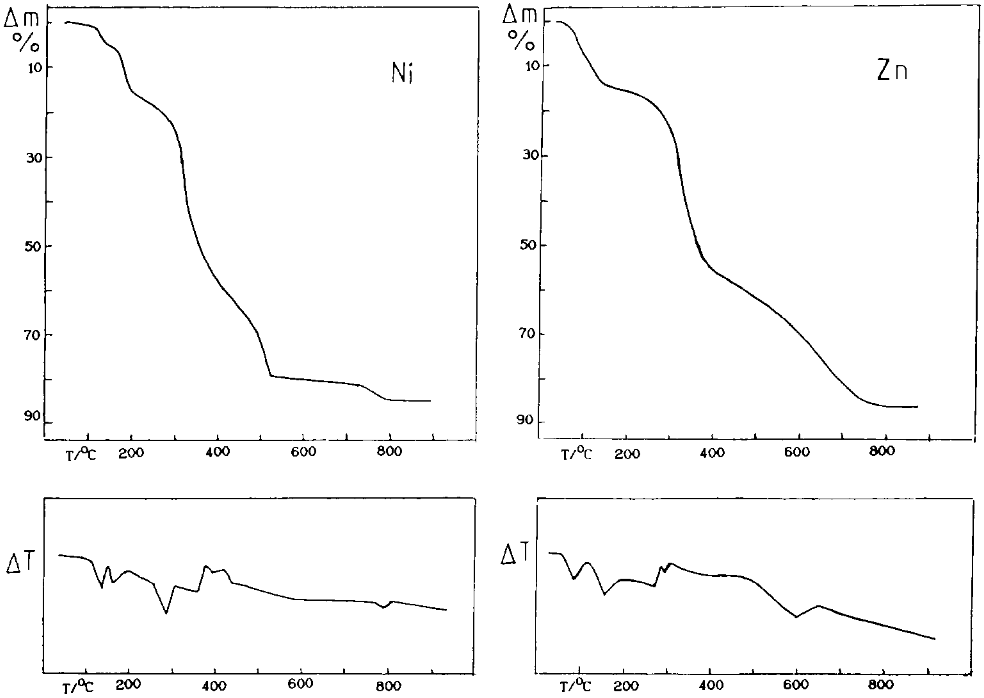

Fig. 2. TG and DTA curves of $(RH)_2M(SO_4)_2 \cdot 4H_2O$ (where M is Ni or Zn).

Stage 1 (34–219°C)

$(RH)_2Zn(SO_4)_2 \rightarrow 4H_2O + (RH)_2Zn(SO_4)_2$

Mass loss: found, 16.20%; calculated, 15.88%.

Stage 2 (219–384°C)

$(RH)_2Zn(SO_4)_2 \leftarrow ZnSO_4 \cdot R + R + H_2SO_4$

Mass loss: found, 37.92%; calculated, 35.07%.

Stage 3 (384–875°C)

$ZnSO_4 \cdot R \rightarrow ZnO + SO_3 + R$

Mass loss: found, 31.42%; calculated, 31.1%.

M(II) is Cd (M_r *= 500.77)*

The thermal decomposition of the Cd compound (Fig. 3, Cd TG curve) takes place in the four stages. In the first step of stage 1, the compound loses one molecule of water and melts (mass loss: up to 108°C, 3.38%; calculated, 3.60%). In the second step of stage 1 from 108 to 213°C, the compound

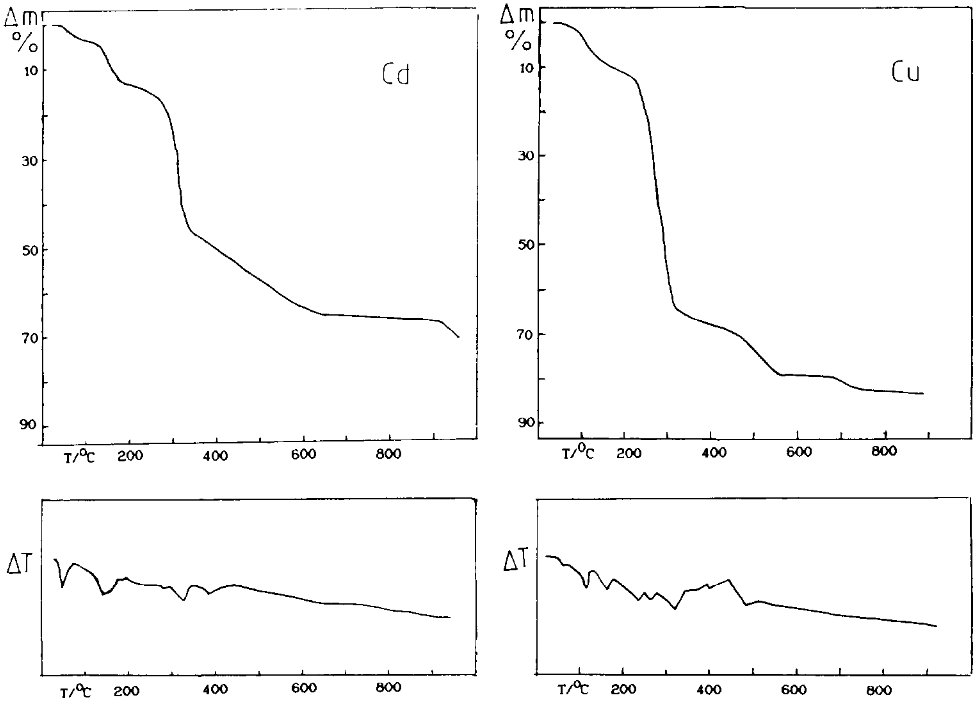

Fig. 3. TG and DTA curves of $(RH)_2M(SO_4)_2 \cdot 4H_2O$ (where M is Cd or Cu).

loses the remaining three water molecules. In stage 2, the anhydrous double salt decomposes to the amine complex $CdSO_4HOCH_2CH_2NH_2$, losing one molecule each of 2-ethanolamine and sulfuric acid. In stage 3 (which takes place over a wide temperature interval), the amine complex obtained loses the remaining one molecule of 2-ethanolamine, and cadmium(II) oxisulfate is obtained. In stage 4, Cd(II) oxisulfate decomposes further to cadmium(II) oxide. The presence of CdO in the residue is confirmed by the X-ray powder diffraction pattern (File No. 5-640 [15]).

Stage 1 (42–213°C)

$(RH)_2Cd(SO_4)_2 \cdot 4H_2O \rightarrow 4H_2O + (RH)_2Cd(SO_4)_2$

Mass loss: found, 14.17%; calculated, 14.39%.

Stage 2 (213–350°C)

$(RH)_2Cd(SO_4)_2 \rightarrow CdSO_4 \cdot R + R + H_2SO_4$

Mass loss: found, 31.86%; calculated, 31.78%.

Stage 3 (350–666°C)

$2CdSO_4 \cdot R \rightarrow Cd_2OSO_4 + 2R + SO_3$

Mass loss: found, 18.55%; calculated, 20.20%.

Stage 4 (666–972°C)

$Cd_2OSO_4 \rightarrow 2CdO + SO_3$

Mass loss: found, 7.00%; calculated, 7.99%.

M(II) is Cu ($M_r = 451.90$)

The dehydration of the Cu compound (Fig. 3, Cu TG curve) takes place in a different manner than the other compounds in this series. The four water molecules leave in two steps: two water molecules leave in the first step; departure of the other two is very closely related to the thermal decomposition of the anhydrous double salt. In stage 2 the double salt dihydrate decomposes to copper(II) sulfate, losing the remaining two water molecules and ethanolammonium sulfate. In stage 3 copper sulfate decomposes to copper(II) oxide (Power Diffraction File No. 5-661 [15]). The thermal decomposition of this compound could be expressed as follows.

Stage 1 (34–159°C)

$(RH)_2Cu(SO_4)_2 \cdot 4H_2O \rightarrow 2H_2O + (RH)_2Cu(SO_4)_2 \cdot 2H_2O$

Mass loss: found, 8.62%; calculated, 7.97%.

Stage 2 (159–331°C)

$(RH)_2Cu(SO_4)_2 \cdot 2H_2O \rightarrow CuSO_4 + 2H_2O + (RH)_2SO_4$

Mass loss: found, 55.61%; calculated, 56.70%.

Stage 3 (331–901°C)

$CuSO_4 \rightarrow CuO + SO_3$

Mass loss: found, 18.45%; calculated, 17.72%.

In the case of the above compounds, it is very difficult to find any regular correlation between the temperature at which dehydration takes place and the difference in the ionic radii of M(II) and the monovalent cation, as was previously suggested [6].

Because it is known that in Tuton's salts, M(II) cations are coordinated with six water molecules, it could be proposed that in the compounds investigated the M(II) cation is coordinated with four water molecules and two OH groups of the ethanolammonium groups, which are potentially donors of electronic couplets. Finding their crystal structures will give the answer.

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