Study of Tutton's Salts (NH₄)₂M(SO₄)₂ · 6H₂O with Mixed Metal Ions in the Structure

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Tutton's salts, $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, in which M represents one, two or three different metal ions in the structure have been obtained previously. Because of similar properties of the transition elements we started to study the system $(NH_4)_2SO_4$—H_2O—MSO_4 (M = Mn, Fe, Co, Ni, Cu, Zn or mixtures of these elements) and we isolated the crystals $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ where M represents mixtures of Ni, Zn; Co, Ni, Zn; Co, Ni, Cu, Zn; Fe, Co, Ni, Cu, Zn; Mn, Fe, Co, Ni, Cu, Zn. The products were characterized by chemical analysis. X-ray powder photographs of the products confirmed that they have structures similar to those of other Tutton's salts. The thermal decomposition of the salts was studied in air and in an argon atmosphere and the final products were identified by X-ray powder photographs.

INTRODUCTION

The hydrated double sulphates (Tutton's salts), $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, where M is Mn or a transition element, were widely investigated in the sixties[1-6]. The structures of the compounds were established by X-ray diffraction analysis which showed that the general packing of the ions and the hydrogen bonded network is essentially identical in all Tutton's salts. The central metal ion is surrounded by six water molecules and each water molecule forms two hydrogen bonds. These range in length from 2.72 to 2.82 Å. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulphate groups; three are normal but one is bifurcated.

Soviet workers have studied the solubility of two or three different Tutton's salts and determined the equilibria between aqueous and solid solutions[7,8]. In our laboratory Tutton's salts with two to six different metal ions were prepared and investigated.

RESULTS AND DISCUSSION

Aqueous solutions of mixed metal sulphates in equi-molar ratios together with ammonium sulphate (50% excess) were mixed and crystals of the formula $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ were isolated. where M = Ni, Zn; Co, Ni, Zn; Co, Ni, Cu, Zn; Fe, Co, Ni, Cu, Zn; or Mn, Fe, Co, Ni, Cu, Zn. The chemical analyses are given in Table I and shows the fraction of the metal ions which crystalized when the solids were harvested.

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* Died in 1983.

TABLE I

Chemical Analysis of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$

$(NH_4)_2M(SO_4)_2 \cdot 6H_2O$	$\%NH_2$	$\%Mn$	$\%Fe$	$\%Co$	$\%Ni$	$\%Cu$	$\%Zn$	$\%SO_4$	$\%H_2O^*$
M = Ni, Zn	9.0				8.7		6.2	49.3	26.8
M = Co, Ni, Zn	9.1			2.7	6.9		4.7	49.7	26.9
M = CO, Ni, Cu, Zn	9.0			2.4	6.1	1.9	4.2	49.3	27.1
M = Fe, Co, Ni, Cu, Zn	9.1		0.87	2.2	5.9	1.6	3.7	49.3	27.3
M = Mn, Fe, Co, Ni, Cu, Zn	9.1	0.32	0.72	2.1	5.8	1.5	3.5	49.4	27.6

*H_2O is calculated as a difference to 100.

On the basis of chemical analysis the molar ratios of the components were calculated and are given in Table II.

TABLE II

Calculated Molar Ratio of $NH_4 : M : SO_4 : H_2O$ (M = 1)

$(NH_4)_2M(SO_4)_2 \cdot 6H_2O$	NH_4	Mn	Fe	Co	Ni	Cu	Zn	SO_4	H_2O
M = Ni, Zn	2.05				0.61		0.39	2.11	6.12
M = Co, Ni, Zn	2.14			0.20	0.50		0.30	2.19	6.32
M = Co, Ni, Cu, Zn	2.08			0.17	0.44	0.12	0.27	2.15	6.30
M = Fe, Co, Ni, Cu, Zn	2.14		0.06	0.16	0.43	0.11	0.24	2.17	6.44
M = Mn, Fe, Co, Ni, Cu, Zn	2.19	0.03	0.06	0.15	0.43	0.10	0.23	2.23	6.67

In the syntheses described, incorporation of a new metal ion in the structure inevitably changes the molar ratio of the metals, but the ratio between any two metals is nearly constant (deviations can be attributed to analytical error).

The X-ray powder photographs of the compounds isolated are identical. It is evident that one metal can be replaced by another without significant effect on the structure.

Thermal decomposition studies show that decomposition occurs in the same way irrespective of the number of metals in the structure. The decompositions were investigated in an inert argon atmosphere and in air. Characteristic TG, DTG and DTA curves of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn) are shown in Figures 1 and 2.

Thermal decomposition of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ in an argon atmosphere (Figure 1) begins at 25 °C. In the first step the sample loses 26.0% of its weight, which corresponds to the loss of water. This step is accompanied by a strong DTA endothermic effect at 165 °C and DTG effect at the same temperature. In the temperature interval between 220 and 500 °C a further 34.4% weight loss occurs, corresponding to formation of metal sulphates. The DTA curve exhibits two exothermic peaks at 270 and 350 °C and two endothermic peaks at 410 and 454°C. In this temperature region ammonium sul-
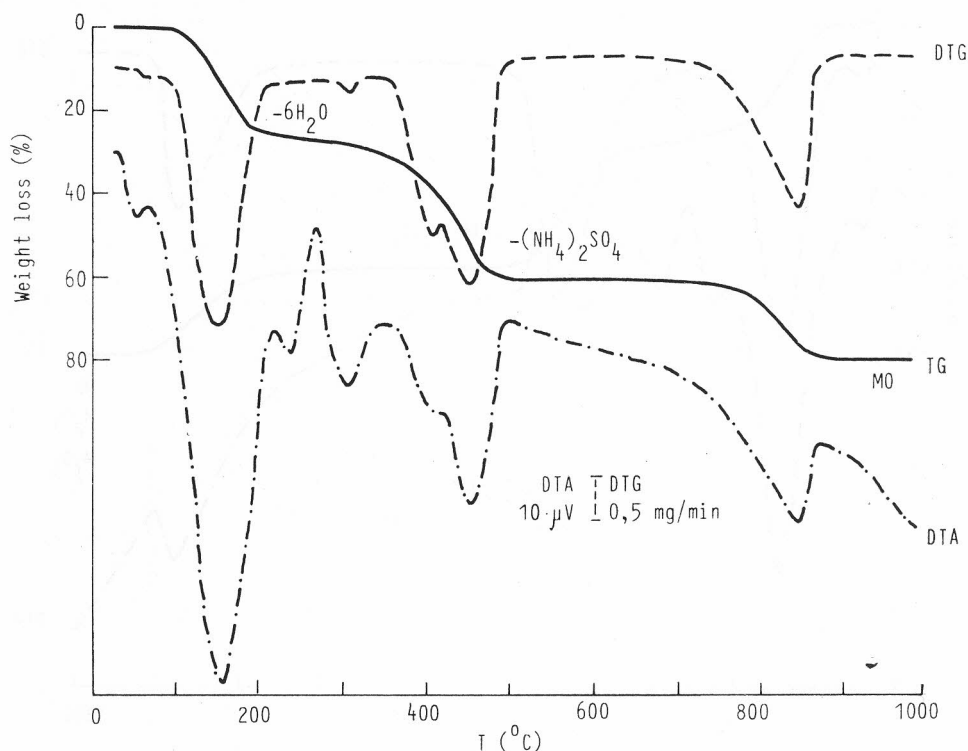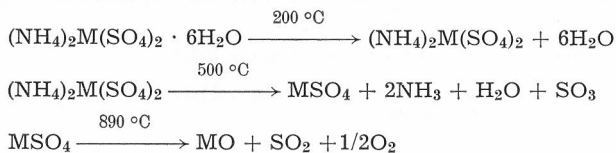
Figure 1. TG, DTG and DTA curves of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn)

Atmosphere: argon — 5 l/h   TG range: 100 mg
Sample weight: 100,00 mg   DTG range: 20 mg/min
Crucible: Pt   DTA range: 200 μV
Heating rate: 8 °C/min   Ref. substance: α-Al$_2$O$_3$

phate is decomposed[9,10]. The exothermic peaks can be explained by partial oxidation of certain metals (Mn, Fe).

In the last step between 500 and 900 °C the sample loses 19.6% of its weight and the total weight loss for the three steps is 80.0%. The decomposition of metal sulphates is accompanied by an endothermic DTA peak and a DTG minimum at 850 °C. Thermal decomposition can be described in terms of the equations:

$$(NH_4)_2M(SO_4)_2 \cdot 6H_2O \xrightarrow{\;200\,°C\;} (NH_4)_2M(SO_4)_2 + 6H_2O$$

$$(NH_4)_2M(SO_4)_2 \xrightarrow{\;500\,°C\;} MSO_4 + 2NH_3 + H_2O + SO_3$$

$$MSO_4 \xrightarrow{\;890\,°C\;} MO + SO_2 + 1/2O_2$$

Thermal decomposition in an atmosphere of air (Figure 2) is different from that in the second step. In the first step the sample loses 26.3% of its weight. In the temperature interval between 215 and 500 °C, where a further 32.8% weight-loss occurs, a mixture of metal sulphates is formed; however,

Figure 2. TG, DTG and DTA curves of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn)

Atmosphere: air — 5 l/h
Sample weight: 100,00 mg
Crucible: Pt
Heating rate: 8 °C/min

TG range: 100 mg
DTG range: 20 mg/min
DTA range: 200 µV
Ref. substance: $\alpha\text{-}Al_2O_3$

Fe^{2+} and Mn^{2+} are oxidized to their higher valences.[11-14] The DTA curve exhibits exothermic effects at 260, 331 and 432 °C and the minimum of the DTG curve is at 420 °C. Between 500 and 925 °C the sample loses 21.0 of its weight and this step is accompanied by peaks in the DTA and DTG curves at 883 °C. The observed total weight loss for the three steps of decomposition is 80.1% and the final product is a solid solution of metal(2+) and (3+) oxides.

Thermal decomposition is described in terms of the equations:

$$(NH_4)_2M(SO_4)_2 \cdot 6H_2O \xrightarrow{215\,°C} (NH_4)_2M(SO_4)_2 + 6H_2O$$

$$(NH_2)_2M(SO_4)_2 \xrightarrow{500\,°C} \begin{array}{l} MSO_4 \\ M_2(SO_4)_3 \end{array} + 2NH_3 + SO_3 + H_2O$$

$$\begin{array}{l} MSO_4 \\ M_2(SO_4)_3 \end{array} \xrightarrow[925\,°C]{} \begin{array}{l} MO \\ Fe_2O_3 \\ Mn_3O_4 \end{array} + SO_2 + 1/2O_2$$

In thermal decomposition studies of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ in argon and in air atmospheres the DTG and TG curves show completion of the decom-

position at 900—950 °C, whereas the DTA curve does not stabilize even at 1000 °C. This can be explained by the phase changes which occur in the compound during the heating process.

The study of the synthesis of $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ with mixed metals provides evidence that several metals can be incorporated into the structure at the same time. The X-ray diffraction patterns show that the salts are solid solutions with structures similar to those of Tutton's salts. The X-ray powder photographs of all starting materials were recorded and compared with those of solids solutions. Their d spacings are distinctly different from d spacings of isolated Tutton's salts.

Studies on Tutton's salts containing mixed metals in ratios which, on thermal decomposition, yield solid solutions suitable for the preparation of ferrites are in progress.

<div align="center">EXPERIMENTAL</div>

Starting materials: The same volumes of 1 M solutions of metal sulphates and a 50% excess of 1 M solution of $(NH_4)_2SO_4$ were mixed and the mixture was acidified with sulphuric acid to prevent hydrolysis. After isothermal evaporation, crystals appeared. They were separated from solution after three hours and dried in air.

Chemical analysis: Ammonium was determined by a direct method[15]. A solution of the ammonium salt was treated with a solution of sodium hydroxide and the mixture distilled. Ammonia was quantitatively expelled and was absorbed in an excess of standard acid. The excess of acid was back-titrated in the presence of methyl red.

The sulphate ion was determined by an indirect complexometric titration[16] after addition of concentrated ammonia solution and a buffer solution (pH 10) using Eriochrome Black T as indicator.

Metals were determined by the atomic absorption spectroscopy[17] in the flames air-acetylene (Zn) and N_2O-acetylene (Mn, Fe, Co, Ni, Cu) on a Varian AA5 Instrument.

The solids were transferred to Pyrex capillaries and X-ray powder photographs were taken with a Debye-Scherrer type camera and $CuK\alpha$ or $FeK\alpha$ radiation.

Thermal analysis was studied on a Mettler TA 1 Thermoanalyzer.

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POVZETEK

Tuttonove soli

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Tuttonove soli $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, kjer M predstavlja enega, dva ali tri različne kovinske ione v strukturi, so bile že izolirane. Z ozirom na podobne lastnosti elementov prehoda smo začeli raziskovati sistem $(NH_4)_2SO_4$—H_2O—MSO_4 (M = Mn, Fe, Co, Ni, Cu, Zn in zmesi teh elementov). Izolirali smo kristale $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, kjer M predstavlja zmes Ni, Zn; Co, Ni, Zn; Co, Ni, Cu, Zn; Fe, Co, Ni, Cu, Zn ali Mn, Fe, Co, Ni, Cu, Zn. Produkte smo karakterizirali s kemijsko analizo. Rentgenski praškovni posnetki spojin so potrdili, da imajo le-te strukturo podobno Tuttonovim solem. Študirali smo tudi termične razkroje spojin v atmosferi zraka in argona in končne produkte opredelili z rentgenskimi praškovnimi posnetki.