

Double sulfates of cobalt(II), nickel(II), copper(II) and zinc(II) with trimethylammonium cation: synthesis, identification and thermal decomposition

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Abstract

Double sulfates of Co(II), Ni(II), Cu(II) and Zn(II) were obtained by evaporation of the reaction mixture of the corresponding metal sulfate and trimethylammonium sulfate aqueous solution in molar ratio 1:6, at room temperature. The crystals obtained were identified and investigated by elemental analysis, TG, DTG and DTA analysis, X-ray powder diffraction and electronic spectroscopy. It was found that the double sulfates of Co(II), Ni(II) and Zn(II) have the general empirical formula $[(\text{CH}_3)_3\text{NH}]_2\text{M}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, but although obtained in the same manner, the double sulfate of copper has the empirical formula $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$. The X-ray powder diffraction patterns of the compounds obtained, show that the double sulfates of cobalt and zinc are isostructural, but although it has the same empirical formula, the double sulfate of nickel seems not to be isostructural with them. The thermal decomposition of the compounds is also discussed.

INTRODUCTION

The double sulfates of M^{2+} with M^+ and NH_4^+ have been investigated from many different points of view. However, up to now, there has been little data concerning the double sulfates of divalent metal cations with monovalent organic cations. Investigations have been carried out on the double sulfates of the divalent transition metals with the hydrazinium cation [1–3]. Recently, we have reported the synthesis and some investigations on the double sulfates of manganese and cadmium with the monomethylammonium cation [4], and also the synthesis, identification and thermal decomposition of double sulfates of Co(II), Ni(II), Cu(II) and Zn(II) with the monomethylammonium cation [5]. It is very interesting that although the general formula of the above compounds is the same as the general formula of the isomorphous series of Tutton salts $(\text{M}_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$, they are not isomorphous with them. This was

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confirmed by determination of the crystal structure of double sulfates of cobalt and copper with the monomethylammonium cation [6]. The crystals are triclinic, space group, $\bar{P}1$ with $Z = 1$, in contrast to Tutton salts which are monoclinic, space group $P2_1/a$ with $Z = 2$.

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

EXPERIMENTAL

Procedure

Double sulfates of cobalt, nickel, copper and zinc with the trimethylammonium cation were obtained by evaporation of the reaction mixture of the corresponding metal sulfate and trimethylammonium sulfate aqueous solution in molar ratio 1:6. The crystal products were filtered off, washed with ethanol and dried in air.

The compounds obtained were characterised and investigated by X-ray powder diffraction, TG, DTG and DTA analysis, elemental analysis and electronic spectroscopy.

Apparatus and methods

The X-ray diffraction patterns were obtained on a Jeol-diffractometer, model JDX-7E, by $\text{Cu K}\alpha$ radiation, Ni-filtered with a goniometer model DX-GO-F. The d values were corrected with $\alpha\text{-SiO}_2$.

TG, DTG and DTA curves were obtained on Mettler thermoanalyser, Model T1 in a flow of dry air. Experimental conditions: reference substance for DTA determination $\alpha\text{-Al}_2\text{O}_3$, TG macrosample holder with platinum crucibles, heating rate 4 K min^{-1} in the temperature range 293–973 K.

Electronic spectra were recorded on an HP 8452A spectrophotometer with photo diode array, in a Nujol suspension.

Quantitative determinations of C and H were carried out according to Liebig's method on a Coleman Model 33 analyser, and N was determined by the method of Dumas. Complexometric methods were used for quantitative determination of the metals.

The compounds were charred to oxides in a furnace at 900°C .

RESULTS AND DISCUSSION

According to the results of the elemental and TG analysis of double sulfates of cobalt, nickel and zinc with trimethylammonium cation (Table 1), it could be concluded that their general empirical formula is $[(\text{CH}_3)_3\text{NH}]_2\text{M}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (where M is Co, Ni and Zn). However,

TABLE 1

Results of elemental and thermal analysis of $[(\text{CH}_3)_3\text{NH}]_2\text{M}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (where M is Co, Ni, Zn) and $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$

		Co/%	Ni/%	Zn/%	Cu/%
		515.42 ^a	515.19 ^a	521.85 ^a	661.61 ^a
M ²⁺	Theor.	11.43	11.39	12.53	19.21
	Exper.	11.55	11.31	12.55	19.00
C	Theor.	13.98	13.99	13.81	10.89
	Exper.	14.20	14.00	14.36	10.03
H	Theor.	7.04	7.04	6.95	5.19
	Exper.	7.62	8.00	7.35	5.64
N	Theor.	5.43	5.44	5.37	4.23
	Exper.	6.00	5.81	6.34	5.37
H ₂ O	Theor.	27.96	27.97	27.62	19.21
	Exper.	28.82	28.90	27.35	19.30
TMAS ^b	Theor.	41.96	41.98	41.45	32.69
	Exper.	37.15	38.87	39.12	33.56
MSO ₄	Theor.	30.07	30.04	30.93	48.25
	Exper.	33.34	32.23	33.53	47.14
MO	Theor.	15.57 ^c	14.50	15.59	24.04
	Exper.	16.00	14.27	15.30	24.13

^a M_r , relative molecular mass.

^b TMAS is trimethylammonium sulfate.

^c The oxide obtained for the cobalt compound at 900°C is Co₃O₄.

although obtained in the same manner, the double sulfate of copper has the empirical formula $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (Table 1).

From the X-ray powder diffraction patterns of the compounds obtained, it could be concluded that the double sulfates of cobalt and zinc are isostructural, but although it has the same empirical formula, the double sulfate of nickel is not isostructural with them (Fig. 1). This very strange phenomenon could probably be explained in terms of the effective ionic radii. Thus, according to the data for the effective ionic radii taken from the paper of Shannon [7], where the oxidation state, coordination number and spin state were considered, the ionic radii of cobalt and zinc are very similar (740 and 745 pm respectively), but that of nickel is noticeably smaller (690 pm).

To obtain some data about the crystal structure of these compounds we have procured monocrystals of the copper and zinc double salts whose crystal structure determination is in progress. Also we have recorded the electronic spectra of the cobalt and nickel salt, which were compared with the electronic spectra of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ respectively, obtained under the same experimental conditions. The spectra were recorded in solid state in Nujol suspension. As can be seen (Fig. 2), the

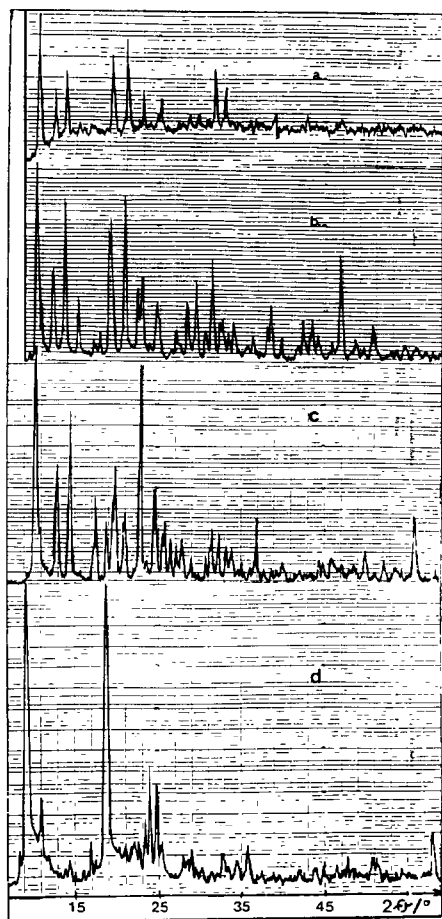


Fig. 1. X-Ray powder diffraction patterns of $[(\text{CH}_3)_3\text{NH}]_2\text{M}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (curve a, Co; curve b, Zn; curve c, Ni) and of $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (curve d).

absorption maxima of both double salts are on the same wavelengths as in the corresponding metal(II) sulfates; therefore it can be concluded that Co(II) and Ni(II) cations in each double salt are coordinated with six water molecules, as well as in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. This indicates that there are at least two different types of water in the double salts with general formula $[(\text{CH}_3)_3\text{NH}]_2(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (where M is Co, Ni and Zn), six of which are co-ordinated to the metal, and two of which are out of the coordination sphere.

The thermal decomposition of these compounds was investigated in the temperature range 293–973 K, in a flow of dry air (Fig. 3). The thermal decomposition of double salts of cobalt, nickel and zinc is very similar and takes place, in general, in two stages. In the first stage, dehydration occurs in two steps in the temperature range 303–428 K for the cobalt compound

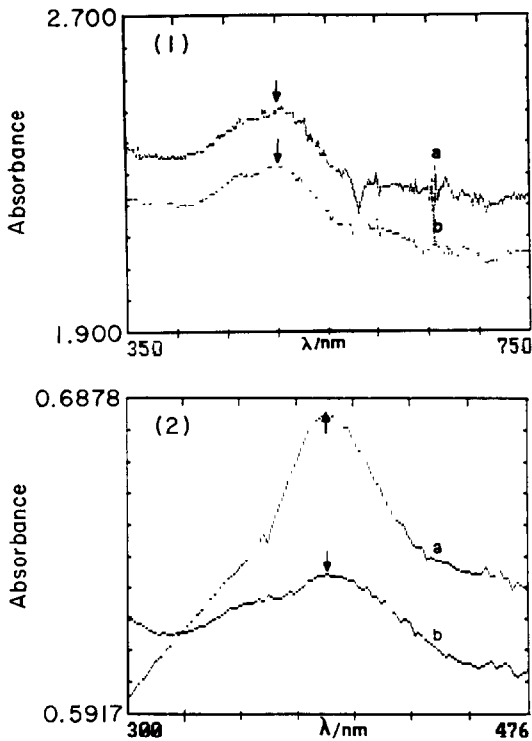


Fig. 2. Electronic spectra of (1) $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (curve a) and $[(\text{CH}_3)_3\text{NH}]_2\text{Co}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (curve b); (2) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (curve a) and $[(\text{CH}_3)_3\text{NH}]_2\text{Ni}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (curve b).

with a maximum on the DTG curve at 403 K, from 323 to 453 K for the nickel compound with maxima on the DTG curve at 358 and 413 K, and from 313 to 413 K for the zinc compound with maxima on DTG at 348 and 393 K. The maxima on the DTA curves are at 353 and 401 K for the cobalt compound, at 358 and 413 K for the nickel compound and at 333 and 393 K for the zinc compound. The calculated and found percentages of water from the TG analysis are given in Table 1.

The first endothermic peak in the stage of dehydration is also connected with the dissolution of the compounds in the water of crystallisation. The temperatures of the experimentally obtained “melting points” (351 K for the cobalt, 358 K for the nickel and 330 K for the zinc double salt) are in good agreement with the temperatures of the first endothermic peak. Considering that the dehydration occurs in more steps (DTG and DTA curves), it could be supposed that there are at least two differential types of water in these compounds, which is in good agreement with the results of the obtained electronic spectra. Because the dehydration of nickel compound begins at higher temperature than the others, and also because of the highest melting point of the nickel compound, it could be assumed that the stability of these compounds increases in the series $\text{Ni} > \text{Co} > \text{Zn}$.

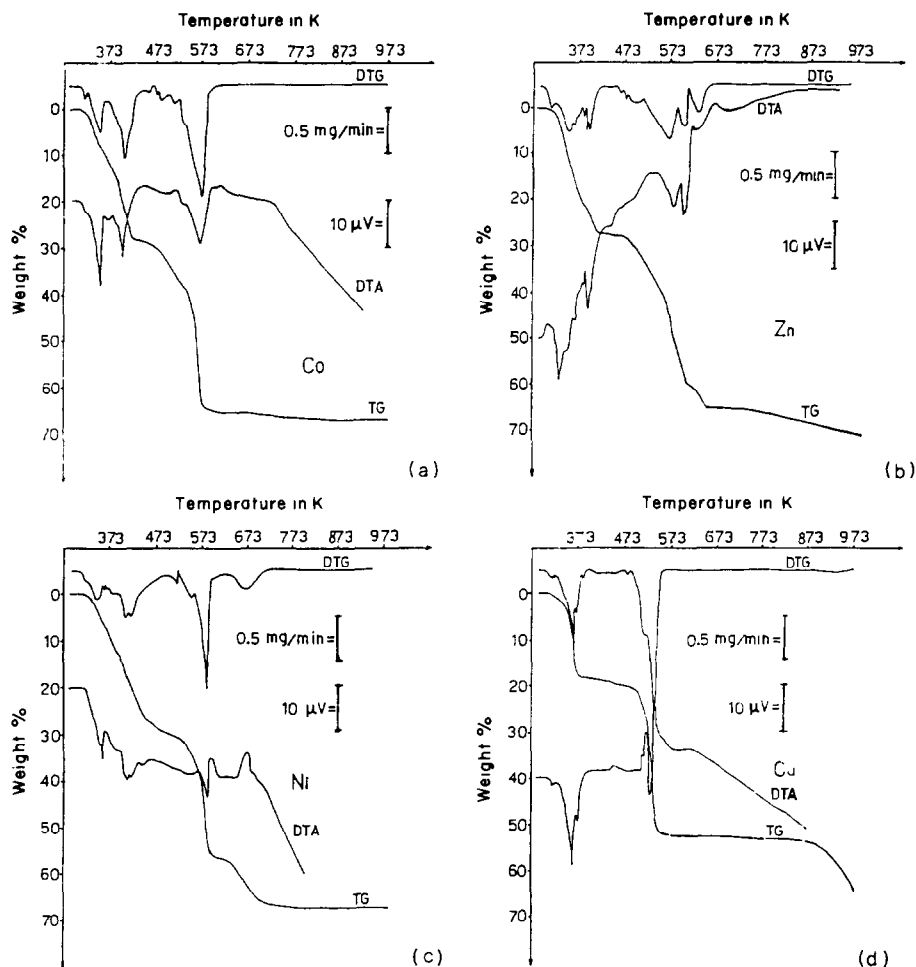


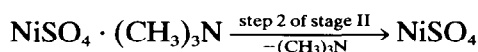
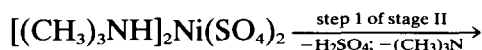
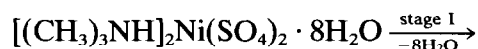
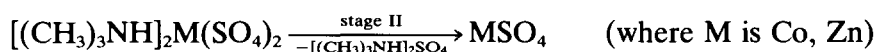
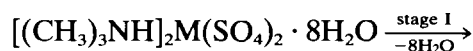
Fig. 3. TG, DTG and DTA curves of $[(\text{CH}_3)_3\text{NH}]_2\text{M}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, (a) M is Co; (b) M is Zn; (c) M is Ni; and of $[(\text{CH}_3)_3\text{NH}]_2\text{Cu}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (d).

This could again be explained by the effective ionic radii of these cations. As was mentioned, the effective ionic radius of nickel is the smallest, so the effective charge has to be greater in comparison with cobalt and zinc. Therefore the M–O bond would be the strongest in the nickel salt in comparison with those of the cobalt and zinc salts.

In the second stage of decomposition the anhydrous double salt decomposes to the corresponding metal sulfate. This stage takes place in the temperature range 443–673 K, for the cobalt salt, from 485 to 723 K for the nickel salt, and from 453 to 683 K for the zinc salt, with an evaluation of trimethylammonium sulfate (according to the literature data, the decomposition of the trimethylammonium sulfate takes place in the temperature

range 543–603 K [8]). This stage takes place only in one step for the cobalt and zinc compounds, but in the case of the nickel compound, an intermediate appears, probably $\text{NiSO}_4 \cdot (\text{CH}_3)_3\text{N}$, which is stable in the short temperature range 603–613 K. This compound decomposes to nickel sulfate (theor. 12.31%; exp. 10.96%). The experimental values (Table 1) for trimethylammonium sulfate are somewhat smaller than the theoretical values, but for the residue of the thermal decomposition (MSO_4) are somewhat greater. This is probably due to the carbon remaining from trimethylammonium sulfate. To check this supposition, we charred the compounds to oxides, in a furnace at 900°C. The experimental values for the oxides are in very good agreement with the theoretical values (Table 1).

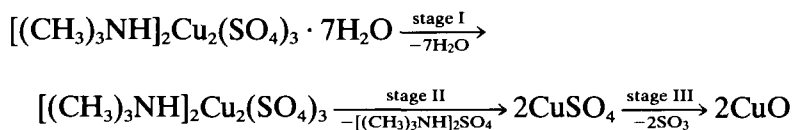
In general the thermal decomposition of these three compounds can be expressed as



Thermal decomposition of the copper salt, also takes place in two stages. The first stage, which corresponds to dehydration, generally takes place in one step, with maximum on the DTG curve at 363 K and at 358 K on the DTA curve. This endothermic peak is due only to dehydration, and is not connected with dissolution of the compound in the water of crystallisation as in the case for cobalt, nickel and zinc salts.

In the second stage, the decomposition of the anhydrous double sulfate occurs in the temperature range 473–553 K, with the maximum on the DTG curve at 543 K. At the same temperature there is an endothermic peak on the DTA curve, but there is also an exothermic peak at 553 K, probably due to the oxidation of the carbon to CO_2 . The final product of thermal decomposition is copper(II) sulfate which is stable in the temperature range 543–873 K, and then decomposes to CuO , which is in agreement with the literature data [9]. The calculated and experimentally found percentages for the water, trimethylammonium sulfate and copper(II) sulfate, obtained from the TG analysis are given in Table 1.

The thermal decomposition of the copper salt can be expressed as



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