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SYNTHESIS, IDENTIFICATION AND THERMAL DECOMPOSITION OF DOUBLE SULFATES OF Mn, Cu AND Cd WITH BENZYLAMMONIUM

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Abstract

On evaporation of an aqueous mixture of M(II) sulfate (*M*(*II*)=Mn, Co, Ni, Cu, Zn or Cd) and benzylammonium sulfate in a molar ratio of 1:2 at room temperature in the presence of sulphuric acid, double sulfates of only Mn, Cu and Cd were obtained. The stoichiometries of the compounds were determined by means of elemental and TG analysis. It was concluded that these compounds have the same general formula: $M(C_6H_5CH_2NH_3)_2(SO_4)_2{\cdot}4H_2O$. These compounds have the same stoichiometry as that of the corresponding double sulfates with ethanolammonium cation, but have different crystal structures.

The thermal decompositions of the investigated compounds in the temperature range from ambient temperature up to 1000°C take place in a similar way, in three well-differentiated stages, but with different pathways in the second and third stages. Metal oxides were obtained as final products.

Keywords: benzylammonium, double sulfates, transition metal(II) elements

Introduction

Many data are available on double M(II) sulfates with monovalent cations with the general $M(I)_2M(II)(SO_4)_2{\cdot}6H_2O$, where *M*(*I*)=alkali metal, NH_4 or Tl(I), known as Tutton salts. Investigations of their crystal structures [1, 2] and thermal behaviour [3–5] have been performed in detail. Some data have also been reported on double sulfates of M(II) with non-classical aliphatic monovalent ammonium cations such as hydrazinium [6, 7], and on the thermal decomposition of the Fe(II) compound with ethylene diammonium [8]. We recently published data on the double sulfates of M(II) with the monovalent cations methylammonium [9, 10], dimethylammonium [11], trimethylammonium [12] and ethanolammonium [13].

Continuing our work on the double sulfates of divalent and trivalent metal cations with non-metallic cations, in this paper we report the results of the synthesis and

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the investigations of double sulfates of some transition M(II) elements and the monovalent cation benzylammonium, for which we have not found any data in the literature. Since it is known that the formation and the structure of the double salts depend on the relative sizes of the ionic radii of the two cations [14], it is of interest to obtain double sulfates of M(II) with monovalent cations with relatively large effective radii, such as benzylammonium cation.

The X-ray powder diffraction patterns and the IR spectra, recorded for better identification of the products of the synthesis, are presented here with the aim of investigating the structural similarity of the double sulfates obtained.

Experimental

Synthesis procedure

Double sulfates of M(II) with benzylammonium cation were obtained as crystalline products by evaporation of a concentrated aqueous reaction mixture of M(II) sulfate (0.0035 mol) and benzylammonium sulfate in a molar ratio of 1:2, with the addition of sulfuric acid (0.008 mol) at room temperature. The products were filtered off, washed with methanol and dried in air. Well-defined, large monocrystals were isolated mechanically for further investigations. In order to identify the products and determine their stoichiometry, IR, X-ray powder diffraction, elemental analysis, thermogravimetric (TG) analyses, derivative thermogravimetric (DTG) and differential thermal analyses (DTA) were performed.

Benzylammonium sulfate was obtained by dropwise addition of diluted sulfuric acid (p.a.) to benzylamine (for synthesis) until a pH of about 4 was reached, during constant external cooling with an ice-water bath. The white crystalline product obtained was filtered off and dried in air.

Analytical methods

The X-ray powder diffraction patterns were recorded on a TUR-MM62 instrument (Dresden, Germany), using CoK_{α} radiation and an iron target.

The IR spectra were recorded with a System 2000 FTIR interferometer (Perkin Elmer) in the region 4000–400 cm^{-1}, from Nujol mulled solid samples placed between KBr pellets.

TG, DTG and DTA were performed on a Q Derivatograph (MOM, Hungary) in a static air atmosphere at a heating rate of 10°C min^{-1}, with samples of about 100 mg in Pt crucibles. The reference substance was pure alumina.

Elemental analyses of carbon and hydrogen were carried out on a Coleman Model 33 instrument by Liebig’s method, while the nitrogen content was determined by the Dumas method.

Results and discussion

General considerations

The results of X-ray powder diffraction analysis of the products of the syntheses allowed the conclusion that only Mn, Cu and Cd formed double sulfates, while only the starting compounds were recovered in the cases of the attempted syntheses with the sulfates of Co, Ni and Zn. By means of elemental (Table 1) and TG analyses, the general formula of these double sulfates was found to be closest to $M(C_6H_5CH_2NH_3)_2(SO_4)_2\cdot 4H_2O$ (*M*=Mn, Cu or Cd). Their stoichiometry is identical to that of the isostructural series of double sulfates of M(II) (*M*=Mn, Co, Ni, Cu, Zn or Cd) with ethanolammonium cation (which is also a cation of large size) [13], but their crystal structures are different. From our continuous investigations on the double salts of various M(II) ions, it could be inferred that the number of water molecules in the crystal structure depends on the relative sizes of the two cations.

Table 1 Results of elemental analyses of $M(C_6H_5CH_2NH_3)_2(SO_4)_2\cdot 4H_2O$ and determination of water content (1st decomposition stage) from the TG curve (in mass%, found/calculated)

M(II)	C	H	N	H_2O
Mn	31.3/31.4	4.8/5.3	5.0/5.2	14.0/13.5
Cu	30.1/30.9	5.3/5.2	5.4/5.2	14.0/13.2
Cd	27.6/28.3	4.7/4.8	4.5/4.7	12.1/13.0

Table 2 Characteristic infrared frequency data[a] for benzylammonium sulfate (BAS) and $M(C_6H_5CH_2NH_3)_2(SO_4)_2\cdot 4H_2O$ (*M*=Mn, Cu or Cd) double sulfates

Compound				Approximate assignment
BAS	Cu	Cd	Mn	
	3580–2500 b, s	3590–2550 b, s	3600–2550 b, s	ν(NH)+ν(OH)+ν(CH)
3310–2240 b, s				ν(NH)+ν(CH)
	2412 w	2370 w	2394 w	
2145 w, b	2088 w, b	2065 w, b	2052 w, b	NH_3 (combination)
	1673 w	1662 w	1668 m	δ(H_2O)
1616 s	1625 m	1626 m	1628 m	benzenoid
1513 s	1530 s	1520 s	1520 s	
1217 w	1218 w	1217 w	1218 w	
1200–815 vs	1200–1000 vs	1200–1000 vs	1200–1000 vs	ν(SO_2)
	971 s	973 s	974 s	
<800	<800	<800	<800	deformations, librations

[a] The frequencies are given in cm^{-1}. The symbols denote: b – broad, vs – very strong, s – strong, m – medium, w – weak, δ – deformational, ν – stretching

From the X-ray powder diffraction patterns (Fig. 1) and the IR spectra (Table 2), it can be concluded that the crystal structures of the Mn and Cd compounds are similar to each other, but, in spite of the same empirical formula, the crystal structure of the Cu compound is pronouncedly different. The attempts to synthesize the double sulfates of Co, Ni and Zn with the same monovalent cation were unsuccessful and always resulted in recovery of the starting compounds. This seems strange if the effective ionic radii are taken into account. The effective ionic radii (e. g. for the coordination number six) of Cu^{2+}, Mn^{2+} and Cd^{2+} are 0.73, 0.67 and 0.95 Å, respectively, while those for Co^{2+} and Ni^{2+} are 0.79 and 0.70 Å [15] and thus larger than that of Mn^{2+} and smaller than that of Cd^{2+}. This implies that some other structural factor plays a significant role and leads to the observed empirical conclusion.

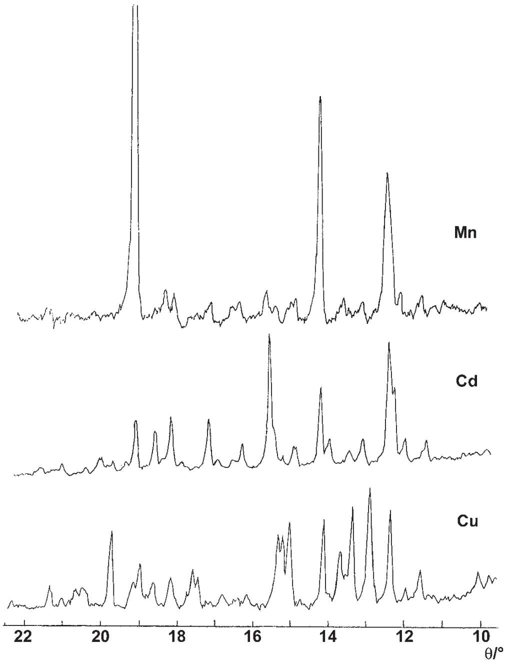

Fig. 1 X-ray powder diffraction patterns of $M(C_6H_5CH_2NH_3)_2(SO_4)_2\cdot4H_2O$

The IR spectra (Table 2) of all M(II) compounds display strong and broad absorptions in the region 3600–2550 cm^{-1}, originating from the OH and NH stretchings, and some weak ν(CH) modes superimposed on the lower-frequency side. Since the parent compound is anhydrous, only the complex NH absorption, in addition to the ν(CH) bands, is present in the region 3310–2240 cm^{-1} of its spectrum. The bands at about 1626 cm^{-1} (1617 cm^{-1} in the spectrum of the parent compound) and 1515 cm^{-1} are found in all spectra in Table 2 and are probably benzenoid modes. A characteristic feature of the higher-frequency band (1617 cm^{-1}) is that it is shifted to higher frequencies (by about 10 cm^{-1}) for all metal salts. The weak bands at around 1670 cm^{-1}, on the other hand, are water deformation modes, which are absent from the spectrum of benzylammonium sulfate itself. The strong and pronouncedly complex absorption in the region 1190–1010 cm^{-1} is attributed to the $\nu(SO_4)$ modes.

Thermal studies

As may be seen from Figs 2–4, the TG curves reveal that the thermal decompositions of the investigated double sulfates occur in three stages. The Mn and Cd compounds decompose in a similar way, but the Cu compound adopts a different pathway.

The dehydration process (the first stage) takes place with different rates (two DTG steps) and is connected with two DTA peaks. This suggests that the crystal water molecules are bonded in different ways. Thus, in this stage two steps could be clearly differentiated in the TG curve of the Mn compound.

The second stage of the thermal decomposition of the Cd and Mn compounds starts at about 220°C, and that of the Cu compound at about 190°C, indicating that the sequence of thermal stability of the anhydrous double sulfates is Cu<Mn<Cd. The second stage (TG curves) takes place in one step (the Cu compound) or in three steps (the Mn and Cd compounds). This may be explained by the fact that the decomposition of the anhydrous Cu compound to copper sulfite takes place in one step and is accompanied by endothermic and exothermic effects. The small endothermic effect

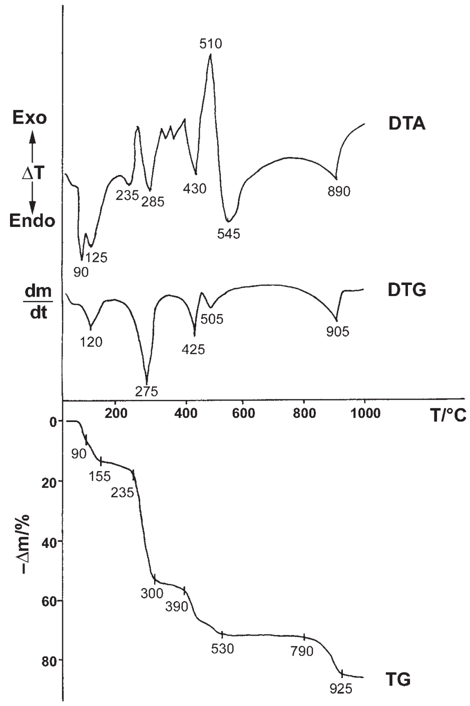

Fig. 2 TG, DTG and DTA curves of $Mn(C_6H_5CH_2NH_3)_2(SO_4)_2\cdot 4H_2O$

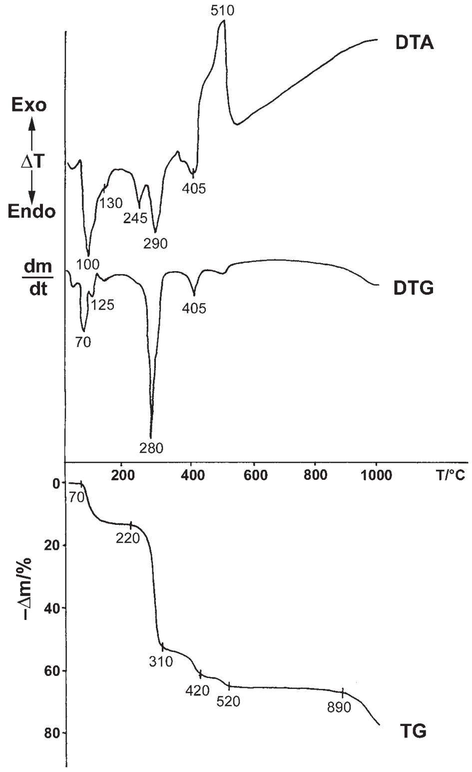

Fig. 3 TG, DTG and DTA curves of $Cd(C_6H_5CH_2NH_3)_2(SO_4)_2{\cdot}4H_2O$

(DTA curves) at 200 (Cu), 235 (Mn) and 245°C (Cd) at the beginning of this stage suggests thermal dissociation of the anhydrous double salt. The strong exothermic effects at about 390°C (the Cu compound) and about 510°C (The Mn and Cd compounds) are related to small mass losses and are possibly a result of redox processes of the organic cations and stabilization of the crystal structures. In addition, in the case of the Cu compound, the mass loss in this stage suggests the evolution of oxygen and subsequent reduction of Cu(II) sulfate to Cu(II) sulfite. The second stage in the thermal decompositions of the anhydrous double sulfates of Mn and Cd is more complicated and takes place in three steps. In the first step in this stage, the compounds lose water and benzylamine, while in the second and third steps, which are not clearly differentiated, sulfur trioxide and M(II) sulfate are obtained. The last step is related to an exothermic effect, which suggests that a redox reaction (similarly to the case of the Cu(II) compound) takes place.

In the third stage, decomposition of the M(II) sulfates or Cu(II) sulfite to the corresponding metal oxides takes place. From the TG curves, it is obvious that Cu(II) sulfite starts to decompose at about 600°C, which is much lower (by about 150°C) than that for Mn(II) sulfate, while the latter decomposes at a lower temperature than

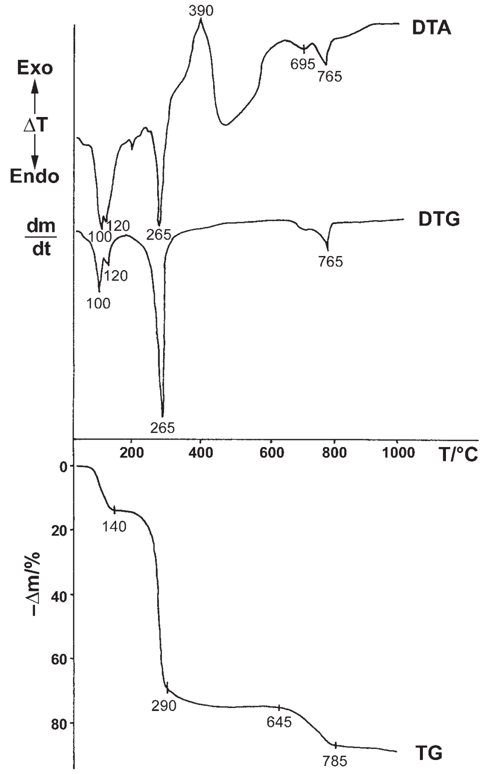

Fig. 4 TG, DTG and DTA curves of $Cu(C_6H_5CH_2NH_3)_2(SO_4)_2{\cdot}4H_2O$

Cd(II) sulfate (by about 100°C). In the case of the decomposition of Cu(II) sulfite, two rates, two peaks in the DTG curve and two endothermic effects, at 695 and 765°C, are apparent. This suggests that the process takes place with the evolution of two different gaseous products, as represented by the equation below.

Decompositions of Cd(II) and Mn(II) double sulfates:

Stage I, dehydration:

$M(C_6H_5CH_2NH_3)_2(SO_4)_2{\cdot}4H_2O \rightarrow M(C_6H_5CH_2NH_3)_2(SO_4)_2+4H_2O(g)$

mass loss for Mn: found 14.0%, calculated 13.5%;
mass loss for Cd: found 13.0%, calculated 12.1%

Stage II, decomposition of M(II) double sulfate:

a) Cd compound:

II-1: $Cd(C_6H_5CH_2NH_3)_2(SO_4)_2 \rightarrow CdS_2O_7+2C_6H_5CH_2NH_2(g)+H_2O(g)$

mass loss: found 38.5%, calculated 37.4%

II-2 and 3: $CdS_2O_7 \rightarrow CdSO_4+SO_3(g)$

mass loss: found 12.5%, calculated 13.9%

b) Mn compound:

II-1: $Mn(C_6H_5CH_2NH_3)_2(SO_4)_2 \rightarrow Mn(HSO_4)_2+2C_6H_5CH_2NH_2(g)$

mass loss: found 40.0%, calculated 39.97%

II-2 and 3: $Mn(HSO_4)_2 \rightarrow MnSO_4+SO_3(g)+H_2O(g)$

mass loss: found 18.0%, calculated 18.3%

Stage III, decomposition of M(II) sulfate:

$CdSO_4 \rightarrow CdO+SO_3(g)$

mass loss: found 11.5% (the decomposition is not finished), calculated 13.98%

$2MnSO_4 \rightarrow Mn_2O_3+SO_2(g)+SO_3(g)$

mass loss: found 14.0%, calculated 13.4%

Decomposition of Cu(II) sulfate:

Stage I, dehydration:

$Cu(C_6H_5CH_2NH_3)_2(SO_4)_2 \cdot 4H_2O \rightarrow Cu(C_6H_5CH_2NH_3)_2(SO_4)_2+4H_2O(g)$

mass loss: found 14.0%, calculated: 13.2%

Stage II, decomposition of the anhydride of Cu(II) double sulfate:

$Cu(C_6H_5CH_2NH_3)_2(SO_4)_2 \rightarrow CuSO_3+2C_6H_5CH_2NH_2(g)+SO_3(g)+H_2O(g)+1/2O_2(g)$

mass loss: found 61%, calculated 60.3%

Stage III, decomposition of Cu(II) sulfite:

$2CuSO_3 \rightarrow Cu_2O+SO_2(g)+SO_3(g)$

mass loss: found 13%, calculated 13.2%

Conclusions

In conclusion, the present work shows that:

- The straightforward synthesis of the double sulfates with the large monovalent benzylammonium cation yielded only the Mn, Cu and Cd salts, with general formula $M(C_6H_5CH_2NH_3)(SO_4)_2\cdot 4H_2O$, while in the cases of Co, Ni and Zn the starting compounds were recovered.

- From the X-ray powder diffraction and IR analyses, it was concluded that the structures of the Mn and Cd compounds are similar to each other, while the crystal structure of the Cu compound is pronouncedly different.
- The thermal decompositions of the Mn and Cd compounds are also similar, but the Cu compound adopts a different decomposition pathway. The dehydration process suggests that the crystal water molecules are bonded in different ways. Further decomposition of the anhydrous salts reveals the following sequence of thermal stability: Cu<Mn<Cd.

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