

ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS

I. STOICHIOMETRY OF THE THERMAL DECOMPOSITION OF $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ AND THE STRUCTURES OF THE INTERMEDIATES FORMED

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The paper deals with the relationship between the crystal and molecular structures of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ on the one hand, and the stoichiometries of their thermal decompositions on the other. With the use of methods of X ray powder diffractograms, i.r. and electronic spectra, evidence is provided that the intermediates of the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ have the same crystal and molecular structures as $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ prepared by other procedures. It is also shown that at temperatures near that of the thermal decomposition, certain, not further identified structural changes take place in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$.

The question of the relationship between the structures of coordination compounds and the courses of their thermal decompositions remains an actual one. Many difficulties encountered in attempts to establish some correlation between the structure of a compound and the course of its thermal decomposition are due to factors making themselves felt in the reactions of heterogeneous systems, which can effect the reaction mechanism, but need not be conditioned, however, by the chemical properties of the compounds in the system under investigation.

For Cu(II) complexes, which, due to the Jahn–Teller effect of pseudoeffect, respectively, exhibit a plastic coordination sphere [1] and are subject to structural changes not only on coordination of different ligands, but also by the action of external influences such as changes of temperature and pressure [2, 3], investigation of the relationship between their crystal and molecular structures usually determined at laboratory temperature, and the reactions of thermal decomposition, can lead to conclusions which are not correct.

This series of papers has the aim of pointing out the relationship between the structures of copper(II) coordination compounds and the courses and stoichiometries of their thermal decompositions, kinetic and thermodynamic parameters and the possibility of structural changes of the starting compound before reaching the decomposition temperature will not be neglected.

This paper deals with the stoichiometry of the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, especially with regard to the structures of the intermediates of this decomposition process. The stoichiometry of the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ has been the subject of many publications, e.g. [4–8], which essentially came to the conclusion that the last water molecule released by the pentahydrate of cop-

per(II) sulphate is that which in the starting compound was not coordinated to the central metal atom. The first doubts about the correctness of the suggested mechanisms of dehydration of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ were voiced in connection with the solution of the structure of $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ [9]. At any event, experimental proof of the fact that $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ separated during the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ are structurally identical with these compounds, but obtained by means of other methods, has not been given till now.

Experimental

Chemicals. $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, p.a. recrystallized twice; H_2SO_4 , p.a. concentrated; methanol, p.a.

Analytical methods. The Cu(II) contents of the prepared compounds were determined by complexometric titration with murexide as indicator. The ratio of Cu: H_2O in the prepared CuSO_4 hydrates was calculated on the basis of the determined Cu(II) content.

Synthesis

The trihydrate of copper(II) sulphate was prepared as an intermediate of the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ on a derivatograph according to [10], and from a methanol solution of the pentahydrate of copper(II) sulphate according to [9].

The monohydrate of copper(II) sulphate was also prepared as an intermediate of the thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ on a derivatograph, the decomposition being interrupted after loss in weight corresponding to the formation of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ had been attained and from a concentrated aqueous solution of CuSO_4 containing 50 wt. % sulphuric acid [11]. The analytical compositions of the prepared substances are listed in Table 1.

Table 1
Analytical compositions of the prepared compounds

% Cu	Complex		$\text{CuSO}_4 \cdot n\text{H}_2\text{O}$			
	$n = 5$	$n = 3$		$n = 1$		
		I	II	I	II	
Theor.	25.45	29.74		35.77		
Exp.	25.47	29.72	29.89	35.35	35.80	

I — prepared by thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

II — prepared by crystallization from solution

Apparatus and measuring methods

Powder diffractograms of the prepared compounds were obtained on a GON-2 diffractograph Czechoslovakia; CuK_α radiation and a Ni filter were used. The powder diffractograms of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ at 50° were obtained with the sample in a metal carrier, the inner part of which was heated by flowing water kept at the necessary temperature in an ultrathermostat. Neither the metal carrier nor the polyethylene sheet closing the carrier with the sample underwent diffraction in the measuring range $2\theta = 5-40^\circ$. Diffractograms were made at 20° , 50° and after cooling, again at 20° for one carrier filling.

The electronic spectra of the prepared compounds were measured with a UNICAM SP 700 spectrophotometer in the region $8000-20\,000 \text{ cm}^{-1}$, using the Nujol suspension technique. To measure the electronic spectra at 50° , the samples were heated to desired temperature in a quartz cell filled with paraffin oil and the spectra were run directly in the cell.

The i.r. spectra were also measured using the Nujol suspension technique, with a Perkin-Elmer 137 spectrophotometer, in the range $650-1700 \text{ cm}^{-1}$.

The thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ was performed on an CD-102 derivatograph (MOM, Budapest). Platinum crucibles with an upper diameter of 14 mm, supplied with the apparatus, were used. The temperature was measured using Pt/Pt-Rh thermocouples.

Results and discussion

Effect of increased temperature on the structure of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

In addition to a slight shift of some diffraction maxima towards lower values of 2θ compared with the pictures taken at 20° (Table 2) (corresponding to lattice dilation by heat), the powder diffractograms of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ measured at 50° exhibit two other changes. On the most intensive diffraction band at $2\theta = 18.75^\circ$ at the temperature of 20° there is a poorly-resolved shoulder; after heating to 50° this becomes an independent diffraction maximum, and a new, not very marked band additionally appears at $2\theta = 21.8^\circ$. Except for the changes in the relative intensities of the diffraction maxima, all the changes caused by increased temperature are reversible in the powder diffractograms of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$.

The electronic spectra of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ were also measured at 20° , 50° and again at 20° . Increased temperature made the maximum of the $d \leftarrow d$ absorption band shift towards the i.r. region, though by a very small value ($\approx 50 \text{ cm}^{-1}$). This change is reversible, and on cooling to 20° the maximum of the $d \leftarrow d$ band returned to its initial value of $13\,000 \text{ cm}^{-1}$. On the basis of the electronic spectra, we suggest that heating does not give rise to any marked change in the structure of the coordination polyhedron. The changes of the powder diffraction patterns at increased temperature, however, allow the conclusion that this compound undergoes certain

Table 2

The positions of the diffraction maxima and their relative intensities in the powder diffractograms of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at temperatures of 20° and 50°

Sample at 20° before heating		Sample at 50°		Sample at 20° after heating	
2θ	relative intensity	2θ	relative intensity	2θ	relative intensity
15.4	0.56	15.35	0.46	15.5	0.49
16.15	0.52	16.05	0.55	16.15	0.61
17.0	0.23	16.9	0.37	17.1	0.47
17.6	0.16	17.6	0.20	17.6	0.26
18.45*	0.32	18.55	0.62	18.6*	0.77
18.75	1	18.70	1	18.75	1
20.85	0.37	20.65	0.46	20.85	0.47
21.65	0.56	21.45	0.47	21.65	0.64
		21.8	0.34		
22.3	0.64	22.2	0.45	22.3	0.45
24.0	0.34	23.9	0.34	24.0	0.32

* Badly-resolved shoulder.

structural changes before decomposition. Accordingly attempts to explain the stoichiometry of thermal decomposition of this compound starting only from its structure at 20° (though this may be very precise) are not sufficient and must lead to incorrect conclusions.

Study of the structures of intermediates of the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and their comparison with the structures of crystalline substances of the same composition

The first intermediate of the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is the trihydrate of copper(II) sulphate. The powder diffraction patterns (Fig. 1a) of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ prepared by thermal decomposition of the initial compound, and those of crystalline $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ (Fig. 1b) are the same within experimental error, and thus the crystal structures of the $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ samples prepared by the two procedures must be very near to each other. Similarly, the powder diffraction patterns of the $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ samples (Fig. 2) prepared by both given procedures are identical except for relative intensities of the diffraction maxima (Fig. 2a, b).

Even on the basis of the powder diffractograms of both types of compounds $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, obtained by the two different ways, it may be stated that there cannot be great differences in the type of bonding of the water molecules between the respective pairs.

This conclusion is also supported by the results obtained from measurements on the i.r. spectra (Table 3). In the measured region two absorption bands were observed, corresponding to the vibrations of the water molecule. Those in the region

of 870 cm^{-1} are assigned to the coordinated water [12], and those between 1500 and 1700 cm^{-1} to the deformation vibrations of the O–H bond. All the studied compounds exhibit the band at 870 cm^{-1} in the i.r. spectra, while $\text{CuSO}_4\cdot\text{H}_2\text{O}$ shows an additional band at 805 cm^{-1} . The fact that only one band, corresponding to the deformation vibrations of the O–H bond, appears in the i.r. spectra of

Table 3

The i.r. spectra of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4\cdot\text{H}_2\text{O}$ (wavenumbers in cm^{-1} ; the bands were assigned according to [12])

Complex	$\nu_1(\text{SO}_4)$	$\rho(\text{H}_2\text{O})$	$\nu_1(\text{SO}_4)$	$\nu_3(\text{SO}_4)$	$\delta(\text{H}_2\text{O})$
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$		875 m, br	985 vw	1100 vs, br	1640 s 1660 s
$\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ I		870 m	980 w	1075 vs 1140 vs	1610 s
$\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ II		870 m	980 w	1070 vs 1150 vs	1610 s
$\text{CuSO}_4\cdot\text{H}_2\text{O}$ I	680 m	806 m 870 m	1020 s	1075 vs 1130 vs 1190 vs	1500 m
$\text{CuSO}_4\cdot\text{H}_2\text{O}$ II	675 m	805 m 870 m	1020 s	1070 vs 1130 vs 1190 vs	1500 m

I – prepared by thermal decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

II – prepared by crystallization from solution

vs – very strong, s – strong, m – medium, w – weak, vw – very weak, br – broad.

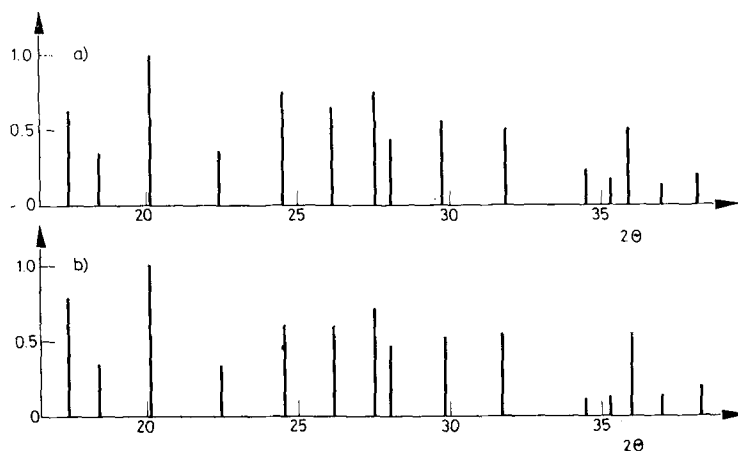


Fig. 1. Powder diffractograms of $\text{CuSO}_4\cdot 3\text{H}_2\text{O}$ prepared: a) by thermal decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$; b) by crystallization from a methanol solution of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

$\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$, indicates that this compound, though prepared in two different ways, contains only equivalent water molecules. In agreement with the structure of $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ [9], in which the symmetry of the SO_4^{2-} group compared with that in $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ is lowered due to the coordination of the sulphate group, a splitting of the $\nu_3(\text{SO}_4)$ vibration takes place; this is still emphasized for $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. At the same time, the intensity of the absorption band corresponding to the $\nu_1(\text{SO}_4)$ vibration also increases, which is forbidden in the tetrahedral SO_4^{2-} ion [13].

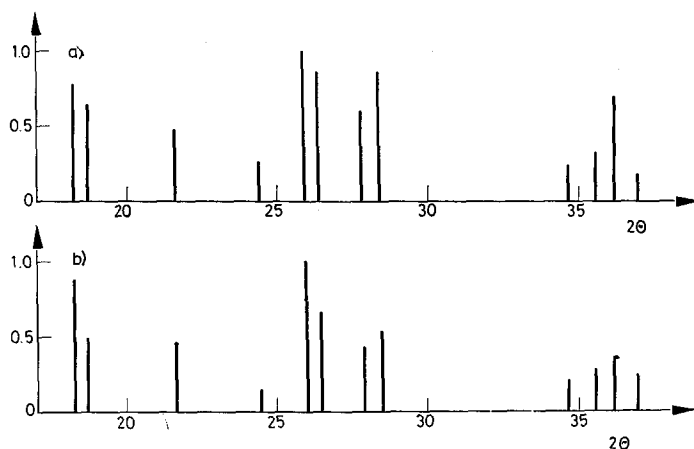


Fig. 2. Powder diffractograms of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ prepared: a) by thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$; b) by crystallization from a solution of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ with 50% H_2SO_4

The i.r. spectrum of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ shows good agreement with the data on the structure of this compound [11], and also with those on the high temperature of decomposition for this compound. It cannot be stated, however, that they would

Table 4

The electronic spectra of the studied complexes

Complex	The maximum of the $d \leftarrow d$ transition, cm^{-1}
$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ — I	12600, 10500 sh
$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ — II	12600, 10500 sh
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$ — I	12200, 9400 sh
$\text{CuSO}_4 \cdot \text{H}_2\text{O}$ — II	12200, 9400 sh

I — prepared by thermal decomposition of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

II — prepared by crystallization from solution

sh — shoulder

support the opinion [14], that in $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ the water molecule reacts with the sulphate anion to form the SO_5H_2 group. The i.r. spectrum of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ as we obtained it is identical with the results in the measured region [15].

The electronic spectra (Table 4) of both intermediates of the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are typical of a tetragonal bipyramidal arrangement of oxygen donor atoms around Cu(II). The splitting of the *d*-orbitals of Cu(II) is somewhat more expressive for $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ than for $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. It may be stated unambiguously that for both types of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and also for both types of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ the ligand field strength around the Cu(II) is the same.

In conclusion therefore it may be stated that even the first intermediate of the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [the trihydrate of Cu(II) sulphate] does not contain any uncoordinated water molecules, since it conforms structurally to $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ prepared from a methanol solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Neither does the further intermediate of this thermal decomposition ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$) contain uncoordinated water molecules.

The experimental results obtained under the experimental conditions used in this work, confirm the assumption of the authors, who solved the structure of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ [9], according to which the opinions as to the mechanism of dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, as represented by the authors of a number of papers, are not correct.

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RÉSUMÉ — L'article examine la corrélation entre les structures cristallines et moléculaires de $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ et $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ d'une part et la stoechiométrie de leur décomposition thermique de l'autre. En se servant des méthodes des diffraction des rayons X sur poudre et des spectres infra-rouges et électroniques on montre que les produits intermédiaires de la décomposition thermique de $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ont les mêmes structures cristallines et moléculaires que celles de $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ et de $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ préparées par d'autres procédés. On montre également qu'à des températures proches de celle de la décomposition thermique de $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ des changements structuraux non encore identifiés ont lieu.

ZUSAMMENFASSUNG — Es wird ein Zusammenhang der Kristall- und Molekularstruktur von $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ und $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ behandelt und andererseits die Stöchiometrie ihrer thermischen Zersetzung. Mit der Auswertung der Röntgen-Pulverdiffraktogramme, der IR- und Elektronenspektren wurde der Beweis erbracht, daß die Zwischenprodukte der thermischen Zersetzung von $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dieselben Kristall- und Molekülstrukturen besitzen, wie auf anderen Wegen hergestelltes $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ bzw. $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. Ferner wurde gezeigt, daß bei Temperaturen in der Nähe der thermischen Zersetzungstemperatur gewisse, jedoch noch nicht identifizierte Strukturänderungen in dem $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ stattfinden.

Резюме — Статья касается взаимосвязи с одной стороны между кристаллическими и молекулярными структурами $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ и $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, а с другой стороны — стехиометрией их термического разложения. Используя метод порошковых рентгенодифрактограмм, инфракрасные и электронные спектры, было доказано, что промежуточные продукты разложения $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ имеют кристаллические и молекулярные структуры аналогичные $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ и $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, которые были получены другими методами. Было также установлено, что при температурах близких к тем, при которых термическое разложение $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ определено, не происходит дальнейшего структурного изменения.