Study of the amorphous product of dehydration of copper(II) sulfate pentahydrate

V. HABER

Department of Inorganic Chemistry, Faculty of Natural Sciences, Charles University, 128 40 Prague

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Dedicated to Professor S. Škramovský on his 75th birthday

X-ray amorphous $CuSO_4 \cdot H_2O$ which is formed at dehydration of $CuSO_4 \cdot 5H_2O$ *in vacuo* was studied. The composition of the dehydration product is not constant, but varies between $CuSO_4 \cdot H_2O$ and $CuSO_4$ depending on dehydration temperature. All these products have irregular arrangement of ions and water molecules which unlike in crystal $CuSO_4 \cdot H_2O$ are not bonded by bridges with two Cu(II) cations.

В работе изучен рентгеноаморфный $CuSO_4 \cdot H_2O$, образующийся при дегидратации $CuSO_4 \cdot 5H_2O$ в вакууме. Состав продукта дегидратации не постоянен, а колеблется между $CuSO_4 \cdot H_2O$ и $CuSO_4$ в зависимости от температуры дегидратации. Все эти продукты имеют неупорядоченное расположение ионов и также молекул воды, которые, в отличие от кристаллического $CuSO_4 \cdot H_2O$, не образуют мостиков между двумя катионами Cu(II).

At dehydration of $CuSO_4 \cdot 5H_2O$ the formation of X-ray amorphous [1] monohydrate [2], which differs from crystalline compound by higher enthalpy [3] and larger surface [4], was observed. These properties can be explained either by a small size of the particles which do not yield sharp diffraction lines or by an irregular arrangement of ions and molecules [3]. This paper presents the results of investigation of the amorphous product by spectral methods, which can contribute to clarification of the character of amorphous $CuSO_4 \cdot H_2O$.

Experimental

$CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5D_2O$ were prepared by free recrystallization of the commercial chemicals, or anhydrous sulfate in D_2O. Isothermal dehydration was performed on quartz spiral *in vacuo* 10^{-1} to 10^{-2} Pa. Sample weights were between 200—300 mg and were checked by weighing; accuracy of reading the dehydration speed was ±0.05 mg/h [5].

Diffractograms of the samples sealed in capillaries were obtained using Mikrometa instrument with CuK_α radiation. Surface areas were determined by thermal desorption method [6]. Infrared spectra in the region 400—4000 cm^{-1} were measured in Nujol suspension between KBr or AgCl windows using an instrument UR-10 (Zeiss, Jena). It was checked whether the sample does not react with KBr. ^{1}H-n.m.r. spectra were measured at 15 and 60 MHz on a spectrometer BS 477 Tesla equipped with the adapter for broad lines [7]. E.s.r. spectra were recorded on a Jeol JES-3DQ instrument in the K region. Diffusion reflection spectra were measured on a spectrometer CF-4 (Optica Milan), in the region 220—950 nm. The measurements were performed at room temperature. All manipulations with the dehydration products were carried out in a dry-box.

Results and discussion

The dehydration of individual crystals and pulverized samples shows similar pattern. After about 50 h the dehydration speed was undetectably low, although the composition of the product was not stoichiometric. Water content in the final products depended only on temperature but not on the particle size. This is illustrated in Fig. 1. The external shape of crystals was preserved at dehydration; their colour was light blue and at temperatures above 80°C blue-grey. The particles of the final products of dehydration were homogeneous; however, if the decomposition was interrupted there was an undecomposed core of pentahydrate inside the particle even if the overall composition of the product was $CuSO_4 \cdot H_2O$ (at 70°C).

All amorphous products are strongly hygroscopic. Sorption of water is accompanied by crystallization of $CuSO_4 \cdot 3H_2O$; only the products with water content $0.1H_2O$ or less give at rehydration $CuSO_4 \cdot 5H_2O$ as does anhydrous $CuSO_4$.

X-ray diffraction of the vacuum products shows only one dark band which according to Ehrenfest equation corresponds to interatomic distance of 0.38—0.41 nm. The product of dehydration of the column cut off from single crystal of $CuSO_4 \cdot 5H_2O$ gives identical diffractogram; the trihydrate formed by

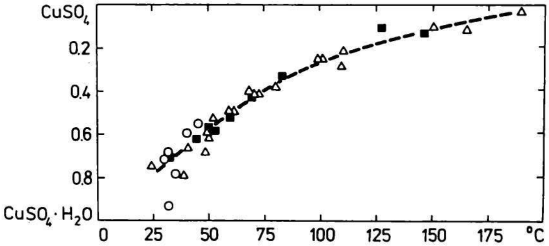

Fig. 1. Temperature dependence of the water content in the products of isothermal dehydration. ■ Single crystal; △ powdered sample; ○ data from Ref. [3].

rehydration does not exhibit preferential orientation of the particles. Infrared spectra of the final products of dehydration are mutually similar as can be seen from Fig. 2 where for comparison also the spectra of crystalline monohydrate, anhydrous sulfate, and of the product of dehydration of pentahydrate in air with the composition $CuSO_4 \cdot 0.5H_2O$, which is apparently a mixture of $CuSO_4$ and $CuSO_4 \cdot H_2O$, are presented. Assignment of bands is shown in Table 1 for several typical samples. Extremely large broadening of the bands corresponding to

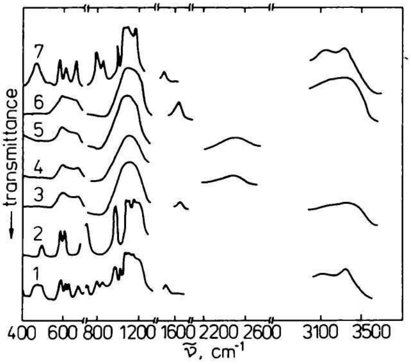

Fig. 2. Infrared spectra of the products of dehydration *in vacuo*.
The spectrum of the product of dehydration in air (bottom curve), crystalline sulfate and monohydrate are also shown for comparison.
1. $CuSO_4 \cdot 0.5H_2O$; *2.* $CuSO_4$; *3.* $CuSO_4 \cdot 0.2H_2O$; *4.* $CuSO_4 \cdot 0.4D_2O$; *5.* $CuSO_4 \cdot 0.7D_2O$; *6.* $CuSO_4 \cdot 0.8H_2O$; *7.* $CuSO_4 \cdot H_2O$.

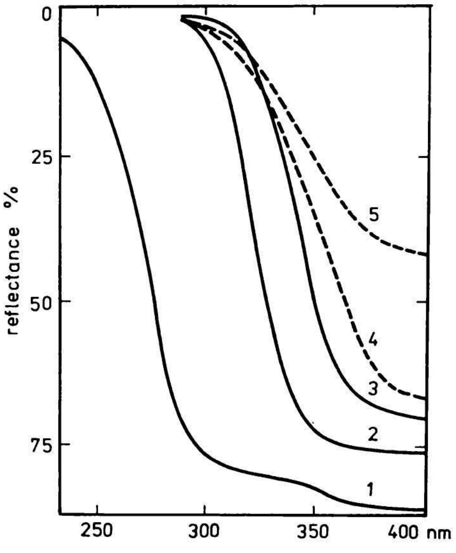

Fig. 3. Diffusion reflection spectra of $CuSO_4$, its hydrate and amorphous products in the u.v. region.
1. $CuSO_4 \cdot 5H_2O$; *2.* $CuSO_4 \cdot H_2O$; *3.* $CuSO_4$; *4.* $CuSO_4 \cdot 0.49H_2O$; *5.* $CuSO_4 \cdot 0.26H_2O$.

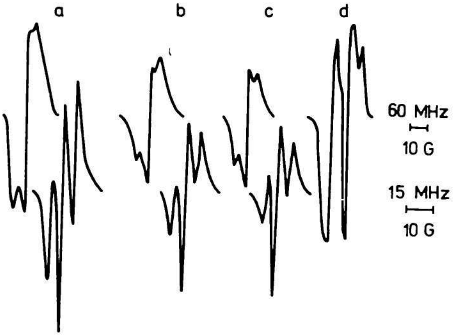

Fig. 4. ^{1}H-n.m.r. spectra of the amorphous products at 15 MHz (bottom) and 60 MHz; for comparison also spectrum of $CuSO_4 \cdot H_2O$ is shown.
a) $CuSO_4 \cdot 0.61H_2O$; *b)* $CuSO_4 \cdot 0.21H_2O$; *c)* $CuSO_4 \cdot 0.10H_2O$; *d)* $CuSO_4 \cdot H_2O$.

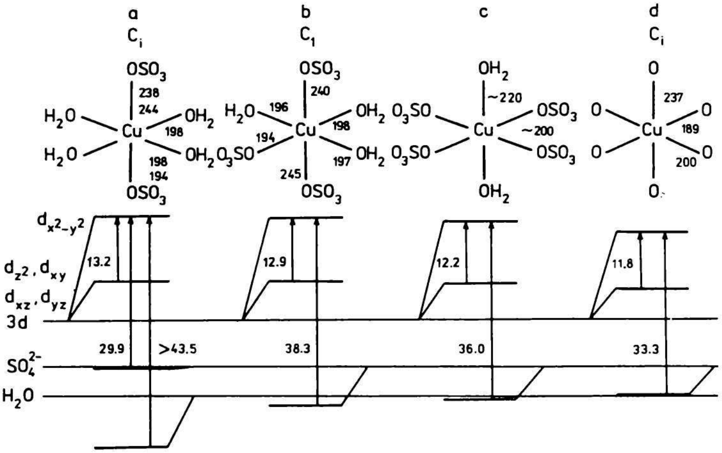

Fig. 5. Environment of Cu(II) and diagram of energy levels in $CuSO_4$ and its hydrates. Below the compound formula site symmetry is shown, the distances are in pm, wavenumbers of maxima in 10^3 cm^{-1}; orbital energies of 3*d* Cu, t_1 (SO_4^{2-}) and b_1 (H_2O) are also presented for comparison. *a*) $CuSO_4 \cdot 5H_2O$; *b*) $CuSO_4 \cdot 3H_2O$; *c*) $CuSO_4 \cdot H_2O$; *d*) $CuSO_4$.

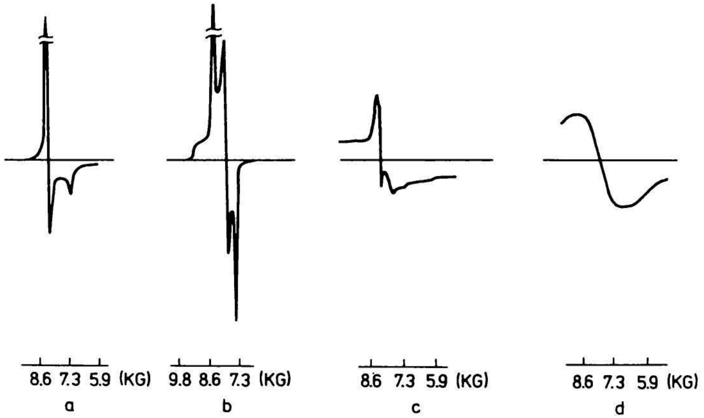

Fig. 6. E.s.r. spectra of cupric sulfate, its lower hydrates and amorphous product dehydrated at 50°C. *a*) $CuSO_4 \cdot 3H_2O$; *b*) $CuSO_4 \cdot H_2O$; *c*) $CuSO_4$; *d*) amorphous product.

stretching vibrations and partially also to deformation vibration $\nu_3(SO_4^{2-})$ can be explained by various ways of coordination which cause different shifts and splittings of vibrations of individual anions. Deformation of sulfate groups apparently varies in a broad range, but is practically independent of the water content at least up to the composition $CuSO_4 \cdot 0.1H_2O$. The position of the stretching vibrations ν(OH) indicates weak hydrogen bridges. Unlike the crystalline monohydrate, in the amorphous products the liberations of water are missing and deformation vibration

Table 1

Infrared spectra of the amorphous products, $CuSO_4$, $CuSO_4 \cdot H_2O$, and assignment of observed bands [5, 8]

Assignment	$CuSO_4 \cdot H_2O$	Amorphous products of dehydration					$CuSO_4$
		$0.8H_2O$	$0.7D_2O$	$0.4D_2O$	$0.2H_2O$	$0.05H_2O$	
$\nu_2(SO_4)$						497 w	496 m
$\varrho(H_2O)$	478 m						
$\nu_4(SO_4)$	593 m	601 m	600 m	600 m	600 m	591 m	589 m
	625 m	661 sh	660 sh	674 sh	670 sh	608 m	609 m
	675 m					673 w	710 m
						705 m	
$\varrho(H_2O)$	805 m						
	870 m						
$\nu_1(SO_4)$	1020 m					973 m	968 s
$\nu_3(SO_4)$	1080 s	1118 s	1110 s	1132 s	1150 s		1083 s
	1120 s					1095 sh	1095 s
	1195 s					1165 s	1155 s
							1210 sh
$\delta(H_2O)$	1510 w	1640 w			1630 w	1625 sh	
$\nu(D_2O)$			2500 m	2490 m			
$\nu(H_2O)$	3135 s	3390 s			3370 m	3370 w	
	3360 s						

s — strong, m — medium, w — weak, sh — shoulder.

$\delta(H_2O)$ exhibits a distinct shift to higher wavenumbers; it is clear that the bridge bonding of water to two Cu(II) cations, characteristic of monohydrate does not take place in the amorphous products. This may be due also to larger Cu—Cu distance in the products as compared to 0.386 nm in $CuSO_4 \cdot H_2O$ [9].

Diffusion reflection spectra of the amorphous products are similar to those of cupric sulfate and its hydrates. The band corresponding to *d—d* transitions at 800—1000 nm as well as the band corresponding to CT transitions $p_\pi \rightarrow 3d_{x^2-y^2}$ in the u.v. region is somewhat broader and with decreasing water content is mildly shifted to longer wavelengths (Fig. 3). It is worth mentioning that the amorphous products with composition $CuSO_4 \cdot 0.4H_2O$ are still distinctly blue while the crystalline monohydrate and anhydrous sulfate are almost white. Wavenumbers of maxima for crystalline compounds [5] are presented in Fig. 5. Shifts in the spectra agree with the position of H_2O and SO_4^{2-} in spectrochemical sequence and with the optical electronegativity values for H_2O (3.5) and SO_4^{2-} (3.2). Bands of the amorphous products overlap the bands of all crystalline compounds. Shape of the spectra in the u.v. region suggests that a part of sulfate ions in the amorphous products is surrounded by sulfate groups only, while blue colour of the products and slowly decreasing shoulder on the short-wave side of the *d—d* transitions band suggest on the contrary coordination of larger number of water molecules on another part of cupric cations.

Comparison of the e.s.r. spectra of lower hydrates and of the amorphous product (Fig. 6) confirms that the amorphous product is not a mixture of these compounds and is in agreement with the assumption of different environments of cations. The width of the band at about 2000 G allows only an estimate of g factor in the range 2.1—2.25. The vacuum products are isotropic since the spectra of dehydrated single crystals practically do not depend on orientation.

Results of measurements of surface areas of the amorphous products are summarized in Table 2.

^{1}H-n.m.r. spectra measured at 15 MHz consist of a narrow central maximum corresponding to more mobile water molecules and broader band which corresponds to more strongly bonded water. It is possible that these maxima correspond to molecules adsorbed on surface and bonded inside the products, since the areas of integrated maxima in Fig. 4 are in approximate agreement with the data in Table 2. The ratio of mobile molecules to rigid ones somewhat increases with increasing dehydration temperature. At 60 MHz frequency both bands strongly overlap. However, the shape of the spectra is quite different from the spectrum of $CuSO_4 \cdot H_2O$, confirming the different ways of water bonding.

Table 2

Surface areas of the amorphous products

In the last column is shown the amount of water in monomolecular layer assuming that one water molecule covers 0.106 nm^2

Dehydration temperature °C	Surface area m^2/g	Total amount of water mol H_2O/mol $CuSO_4$	Water adsorbed on surface mol H_2O/mol $CuSO_4$
40	79.5	0.65	0.22
41	69.5	0.65	0.19
48	81.0	0.58	0.22
60	70.4	0.49	0.18

The existence of amorphous products is probably conditioned by a small mobility of sulfate ions which are coordinated on several different cations and therefore it is difficult for them to regroup in such a way that they fill unoccupied coordination sites formed by removal of water molecules at dehydration. In the amorphous products if compared to $CuSO_4 \cdot H_2O$ at least one apex of coordination polyhedron should be free around each cation due to the different bonding of water. Occupation of these sites by sulfate ions apparently leads to a deformed and metastable arrangement, which at higher temperature or higher water vapour tension which increases mobility of ions [3], regroups to regular crystal lattice. Since the amorphous products are formed also at vacuum dehydration of other hydrates of metal sulfates [4], monohydrates of which have structure similar to that of $CuSO_4 \cdot H_2O$, it is possible to assume in these cases similar mechanism of formation of the amorphous products. However, the difference between crystalline and amorphous compounds is more distinct in cupric compounds, this being probably connected with large variability of internal coordination sphere of cupric cation manifested often by distortion isomerism [10].

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