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Special Review

THERMAL BEHAVIOUR OF HYDRATED COPPER(II) COMPLEXES

Correlation of dehydration steps with structural properties

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Abstract

Dehydration steps of aquacopper(II) complexes with homogeneous and heterogeneous coordination sphere are investigated from the view point of structural changes taking place under their heating to the decomposition temperature and during the dehydration. The role of loosening of intra- and intermolecular hydrogen bonds in the decomposition reaction for the structure changes of the remainder, the structural presumptions of the reactants for lower hydrates formation are discussed.

Activation parameters of dehydration were found to be the lower, the smaller are the structure differences between the reactants and products. They do not reflect the bond length central atom–volatile ligand, much more the overall structure differences between the starting and resulting compounds. From all data on crystal and molecular structures of dehydrated compounds is the reaction pathway best indicated by anisotropic temperature parameters of donor atoms corrected for the thermal movement of the central atom: the higher these values in the bond direction are, the lower the values of activation energies of dehydration are.

Keywords:complexes, hydrated copper(II) complexes, structural properties

Introduction

Although there is no doubt about the existence of an interdependence between the course of the thermal decomposition reactions and the structures of decomposed substances, a lack of a more complex look on these relationships is obvious. The most problematic part of such correlation is the fact that room temperature structures are related to the thermal behaviour of compounds at higher temperatures. This assumption might be correct for compounds with 'rigid' structures, which are not temperature dependent, there is a lot of data showing that with changed temperature the positions of atoms might be varied within the given crystal symmetry, or they can lead to a phase transition, occurring in solid state. The former case represents the situation with so called 'fluxional' complexes of Cu^{II}, for which the local and crystal structures were found to be temperature dependent [1]. In such cases a correlation, made between the room temperature structure and the decomposition course might be incorrect. However, the data on the crystal structures gained at higher than room temperature are really scarce.

The aim of this contribution is to summarize the experimental data on the thermal behaviour of hydrated Cu^{II} complexes showing the importance of

– temperature dependent structure changes, occurring during heating to the decomposition temperature,

– hydrogen bonds for the thermal stability of the compounds and their structures,

– structural presumptions of the decomposed substances for the formation of compounds with lower content of water molecules.

These items are discussed for complexes with homogeneous as well as with heterogeneous coordination sphere, considering the dehydration steps and connected structural changes.

Dehydration of complexes with homogeneous coordination sphere

Compounds, containing six equivalent ligands in the Cu^{II} coordination sphere are not very frequent. These are, however, several hexaquacomplexes, e.g. $M^{I}_{2}[Cu(H_2O)_6](EO_4)_2$, where M^I are NH_4, K, Rb, Cs and Tl, E are S or Se, and $[Cu(H_2O)_6]X_2$, where X^- are $C_6H_5SO_3$, $4\text{-}CH_3C_6H_4SO_3$ and $C_{10}H_{15}OSO_3$, the crystal structures of which are known in most cases [2–5]. Some of these complexes were shown to be fluxional, mainly the $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ [6] and the $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ [7]. In both cases it was found that the Cu^{II} coordination polyhedra, rhombically deformed at lower temperatures change under heating continuously to tetragonally compressed polyhedra. This change occurs via elongation of one pair of equatorial $Cu\text{–}OH_2$ bonds (longer in the rhombically deformed polyhedron) and shortening of the axial $Cu\text{–}OH_2$ bonds, which are the longest ones in the coordination polyhedron. This type of changes was confirmed by our investigation of X-ray powder patterns changes of

$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ under heating [8]. The importance of the lengths of the equatorial Cu–OH_2 bonds for the overall course of the reactions was demonstrated [7, 9, 10] on dehydration steps and corresponding activation parameters of the above mentioned hexaquacomplexes.

The majority of hexaquacopper(II) complexes is decomposed according to the scheme

$$M^I_2[Cu(H_2O)_6](EO_4)_2 \rightarrow M^I_2[Cu(H_2O)_2(EO_4)_2] + 4H_2O \qquad (1)$$

M^I = NH_4, K, Rb, Tl, E = S, Se and $[Cu(H_2O)_6](C_{10}H_{15}OSO_3)_2$ in spite of the fact that the axial Cu–OH_2 bonds are much longer (0.15–0.25 Å) than the equatorial ones at room temperature (Table 1). All hexaquacopper(II) complexes, dehydrated according to scheme (1) possess rhombically deformed coordination polyhedra at room temperature. Taking into account the room temperature structures of the hexaquacopper(II) complexes, the decomposition according to below given scheme (2) would be more natural. Dihydrates, formed in these reactions have five- [11] or hexacoordinated [12] central atoms with coordinated SO_4^{2-} groups, but the monoclinic crystal symmetry is retained. The activation energies found for dehydration according to scheme (1) decrease with the lengthening of the longer pair of equatorial Cu–OH_2 distances (Table 1).

The other $[Cu(H_2O)_6]X_2$ compounds (X^- = $C_6H_5SO_3$, 4-$CH_3C_6H_4SO_3$) [10] as well as the $Cs_2[Cu(H_2O)_6](EO_4)_2]$ (E = S, Se) are dehydrated under formation of tetrahydrates:

$$[Cu(H_2O)_6]X_2 \rightarrow [Cu(H_2O)_4X_2] + 2H_2O \qquad (2)$$

X-ray powder patterns of these complexes taken at elevated temperatures did not show any changes before the dehydration onset [10]. The Cu^{II} coordination polyhedra in these complexes are tetragonal-bipyramidal with all equatorial Cu–OH_2 bonds shorter or near to 2.00 Å (Table 1). Such short Cu–OH_2 equatorial distances occur in seldom compounds, containing planar $[Cu(H_2O)_4]^{2+}$ cations, connected into infinite chains via anionic bridges as in $[Cu(H_2O)_4SO_4]\cdot H_2O$ [13] and $[Cu(H_2O)_4X]$ (X^{2-} = $(CH_3SO_3)_2$, $SO_3(CH_2)_2SO_3$, $SO_3(CH_2)_4SO_3$ [14–16]. Both these structure features are probably needed for the formation of planar $[Cu(H_2O)_4]^{2+}$ moieties. We assume that the difference between energies needed for activation of the very short Cu–OH_2 bonds in the equatorial plane and much longer (0.3–0.4 Å) axial ones is responsible for the different dehydration steps found for tetragonal and rhombic $[Cu(H_2O)_6]^{2+}$ complex cations. These conclusions are supported also by the fact that com-

Table 1 Data on structures and thermal decomposition of complexes with cation $[Cu(H_2O)_6]^{2+}$ and the comparison with analogous Ni^{II} complexes

Compound		Structure data		Thermal decomposition		
		$r(Cu{-}OH_2)$/Å	$\Delta U_{ii}^{1/2}$/Å	Decomp. scheme	E^*/ kJ·mol^{-1}	lg$A$
$M^I_2[Cu(H_2O)_6](EO_4)_2$						
M =	E =					
Na	S			$-4H_2O$	69 ± 4	
NH_4	S	2.2300	0.125	$-4H_2O$	100 ± 5	
		2.0725	0.112			
		1.9660	0.062			
K	S	2.2780	0.104	$-4H_2O$	105 ± 3	
		2.0690	0.104			
		1.9430	0.066			
Rb	S	2.3020	0.080	$-4H_2O$	112 ± 4	
		2.0310	0.084			
		1.9570	0.069			
Tl	S	2.3170	0.092	$-4H_2O$	139 ± 1	
		2.0170	0.096			
		1.9570	0.062			
Cs	S	2.3140	0.088	$-2H_2O$	–	
		2.0040	0.099			
		1.9620	0.057			
NH_4	Se	2.2370		$-4H_2O$	144 ± 4	15.2
		2.0310				
		1.9900				
K	Se	2.2970		$-4H_2O$	124 ± 2	13.4
		2.0440				
		1.9370				
Rb	Se			$-4H_2O$	177 ± 6	20.8
Tl	Se			$-4H_2O$	181 ± 10	21.7
Cs	Se			$-2H_2O$		
$[Cu(H_2O)_6]X_2$, X =						
$C_{10}H_{15}OSO_3$		2.1700		$-4H_2O$	129 ± 7	17.2
		2.0500				
		1.9700				

Table 1 Continued

Compound		Stucture data		Thermal decomposition		
		r(Cu–OH$_2$)/Å	$\Delta U_{ii}^{1/2}$ / Å	Decomp. scheme	E^*/ kJ·mol^{-1}	lg$A$
$C_6H_5SO_3$		2.264, 2.259		$-2H_2O$	142 ± 5	19.2
		1.968, 1.961				
		1.979, 1.958				
$CH_3C_6H_4SO_3$		2.423		$-2H_2O$	111 ± 2	14.8
		1.954				
		1.953				
$M^I_2[Ni(H_2O)_6](EO_4)_2$						
M =	E =					
NH_4	S*	2.05 (2×)		$-6H_2O$	102 ± 5	
		2.03 (4×)				
K	S			$-6H_2O$	111 ± 5	
Rb	S			$-6H_2O$	105 ± 5	
Tl	S			$-6H_2O$	97 ± 5	
NH_4	Se**	2.068		$-6H_2O$	91 ± 3	8.9
		2.055				
		2.043				
K	Se			$-4H_2O$	190 ± 9	23.8
Rb	Se			$-6H_2O$	84 ± 5	7.8
Cs	Se			$-6H_2O$	75 ± 6	7.0
Tl	Se			$-6H_2O$	100 ± 4	10.1

* [59], ** [60], for other references see the text

pounds $M^I_2[Ni(H_2O)_6](EO_4)_2$ with nearly regular octahedral coordination of Ni^{II} are dehydrated in single step [7, 9].

The probability of the cleaving of Cu–OH$_2$ bonds can also be determined on the basis of the values of anisotropic temperature factors of donor atoms corrected for the thermal movement of the central atom in the bond direction:

$$\Delta U_{ii}^{1/2} = (U_{ii}(\mathrm{Cu}) - U_{ii}(\mathrm{O}))^{1/2}$$

The ΔU_{ii} values, reflecting the movement 'freedom' [17] of the axial and longer equatorial Cu–OH$_2$ bonds indicate similar movement freedom for two pairs of water molecules and a much smaller one for the third pair of water molecules in $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$. Although the temperature dependent structural changes of these compounds with alkaline cations are much smaller [6], the ΔU_{ii} values (Table 1) indicate the same situation with the water molecules in these compounds as well. This structure feature may be responsible for the observed decomposition scheme for the hexaquacopper(II) complexes with rhombically deformed coordination polyhedra. The higher the values of activation energies found for the dehydration of these complexes [9] are the lower the $\Delta U_{ii}^{1/2}$ values of the four split water molecules are (Table 1).

Dehydration of compounds with heterogeneous coordination sphere

The role of the inter- and intramolecular hydrogen bonds for the thermal stability of the compounds

Several Cu^{II} aquacomplexes do contain water molecules bonded in their crystals *via* hydrogen bonds. The cleaving of these water molecules is frequently thought to occur without influencing the structure and thermal properties of the remainder. There are experimental data, anyway, indicating considerable structure and stability changes, taking part simultaneously with release of crystal water molecules.

Let us first consider experimental data indicating a decreasing thermal stability of the remainder after crystal water escape. The release of the non-coordinated water molecule [13, 18] from $[CuL_4SO_4]\cdot H_2O$ ($L = H_2O, C_5H_5N$) is connected with quick subsequent or simultaneous decomposition of CuL_4 moiety as well [19, 20]:

$$[Cu(H_2O)_4SO_4]\cdot H_2O \rightarrow [Cu(H_2O)_3SO_4] + 2H_2O$$

$$[Cu(C_5H_5N)_4SO_4]\cdot H_2O \rightarrow [Cu(C_5H_5N)_3SO_4] + H_2O + C_5H_5N$$

The only compound of this type, which does not suffer further decomposition after the release of non-coordinate water molecule is $[Cu(pn)_2SO_4]\cdot H_2O$ (*pn* = $NH_2CH_2CH_2\,CH_2NH_2$) [21] because of the stability of remainder due to chelate bonded neutral ligands and –Cu–OSO_2O–Cu–chains. The decomposition of $[CuBaL]\cdot 2H_2O$ (where *L* is N, N'-ethylenebis(3-hydroxysalicylideneimine)) starts immediately after its dehydration, in spite of the fact that both metal atoms are chelated [22]. The compound $[Cu(en)_2(H_2O)]\,[Ni(edta)]\cdot 3H_2O$

[23] is dehydrated in two steps, in the first one the crystal water molecules being evolved and in the second one the coordinated water molecule [24]. The activation energy for the second dehydration step was found to be lower ($E^* = 48\pm4$ kJ·mol^{-1}) than that for the first dehydration step ($E^* = 78\pm10$ kJ·mol^{-1}) [24].

The changes in the whole chemical bonds network due to the breakdown of hydrogen bonds can be demonstrated on dehydration of some Cu^{II} carboxylate complexes containing both coordinated and crystal water molecules. The crystal structure of copper(II) formate tetrahydrate, for example, consists of double bridged $Cu(HCOOO)_2$ chains held together by an extensive network of hydrogen bonds formed by coordinated water molecules (two to each copper atom) and crystal water molecules, being all placed in one sheet between the copper-formate sheets [25]. The dehydration proceeds under mild temperature and normal pressure in two steps, in both of them two water molecules being evolved [26]. X-ray powder diffraction analysis as well as the IR spectra of the $Cu(HCOO)_2\cdot 2H_2O$ yielded in the first dehydration reaction showed that the α-isomer of this compound was formed [27]. Its structure, however, cannot be simply derived from that of tetrahydrate, because there are two different Cu^{II} coordination polyhedra: $Cu(O_{water})_4(O_{formate})_2$ and $Cu(O_{formate})_6$ [28]. The dehydration of the $[Cu(HCOO)_2(H_2O)_2\cdot 2H_2O$ in vacuo yields the α-$Cu(HCOO)_2$ (royal blue) [29] with pentacoordinated Cu^{II} atoms [30]. Based on these data, one could judge that the dehydration of $[Cu(HCOO)_2(H_2O)_2\cdot 2H_2O$ under normal pressure proceeds also via anhydrous compound formation and its subsequent rehydration. Two experimental facts at least are speaking against this reaction mechanism. The DTG curve of the tetrahydrate dehydration indicates that three reactions occur before the composition $[Cu(HCOO)_2]$ is reached, first two corresponding to a dihydrate formation according to the TG curve. The X-ray powder diffractograms, taken from the cooled down reaction mixture after release of first portions of water indicate the presence of three phases: $[Cu(HCOO)_2(H_2O)_2\cdot 2H_2O$, α-$[Cu(HCOO)_2(H_2O)_2]$ and a third one, which could not be identified as a known one among copper formates [26]. During the dehydration, however, the bonds Cu–O($_{formate}$) as well as Cu–O($_{water}$) were newly formed due to the breakdown of the hydrogen bonds network. The dehydration of $[Cu(sal)_2(H_2O)_2\cdot 2H_2O$ (*sal* = $C_6H_4OHCOO^-$) [31] is not a simple process again, the interconnections between the structures of tetrahydrate [31] and dihydrate [32] being even more complicated than at formates. According to the TG and DTG curves the dehydration proceeds in one step, the anhydrous compound being formed [26] at continuous heating. The only diffracting phase present in the reaction mixture from which 0.6 mol of water escaped [26] was the $[Cu(sal)_2(H_2O)_2]$, according to the X-ray powder analysis [26]. One can conclude that the shape of the TG curve is caused by low thermal stability of the dihydrate, which decomposes simultaneously with the dehydration of the tetrahydrate. We can state that the breakdown of the hydrogen bonds network in this case, analogously to previous ones leads to a considerable restructuring of the whole chemical bonds network. On the other hand, during the thermal dehydration of compound $[Cu(C_2O_4)(NH_3)_2]\cdot 2H_2O$ no significant changes in the mode of coordination of oxalate groups and ammonium molecules were observed [33].

The hydrogen bonds, formed by coordinated water molecules in aquacomplexes are of great importance for the stability of the chemical bonds in the remainder as well. As an example the dehydration of α-$[Cu(HCOO)_2(H_2O)_2]$ can be given [26]. During its dehydration the α-modification of anhydrous copper(II) formate was formed, in which a different scheme of formate groups configuration applies: in the dihydrate one half of them has anti-anti and the other half anti-syn configuration [28], in the anhydrous compound all formato groups do have anti-syn configuration [30]. All these changes occur at relatively low temperature and with low activation energy. However, the pre-exponential factor value indicates structure changes, being much higher than that found for the first dehydration reaction of another modification of $Cu(HCOO)_2\cdot 2H_2O$ (Table 3) [26]. Also the square-planar $[Cu(NH_3)_4]^{2+}$ moieties in $[Cu(NH_3)_4(H_2O)]SO_4$ [34] did not stand the removal of water molecules, which connect them into infinite chains and one from the ammonia molecules is evolved simultaneously with the water molecule [20]. In the early stage of the decomposition of $[Cu(NH_3)_4(H_2O)]SO_4$ the analytical investigation of the reaction mixture showed the composition $Cu(NH_3)_{3.63}SO_4\cdot 0.45H_2O$, evidencing the simultaneous release of water and ammonium molecules [20]. In compounds $[Cu(LL)(H_2O)_2SO_4]$, where *LL* are ethylenediamine, 2,2'-dipyridine and 1, 10-phenanthroline [35–37] are the non-coordinated oxygen atoms from bridging sulfato groups hydrogen bonded either to the ethylenediamine, or in the other two complexes to water molecules. This is reflected in the highest values of activation energy and preexponential factor (Table 2) found for the ethylenediamine complex [38].

The role of the structural presumptions of the dehydrated compound for the formation of a lower hydrate

The formation of a substance with a lower content of volatile ligand has to be in most cases considered as a substitution reaction. The originally non-coordinate outer-sphere anions are coupled to the central atom or they enhance the number of their interactions with one or several central atoms. Anyway, this is not a general way how to rearrange the Cu(II) coordination polyhedra after lowering the number of volatile ligands. In several cases, when the anion binding possibilities are exhausted in the reactant, only symmetry changes of the remaining coordination polyhedra take place. It is obvious that the formation of new bonds by already strongly engaged anions will be more energetically exacting than new bonds formation by anions, only loosely bonded in the reactant. From this point of view it is comprehensible that the dehydration of $CuSO_4 \cdot 3H_2O$ or $CuSO_4 \cdot H_2O$ occur at higher temperatures and with higher activation parameters when compared with the $CuSO_4 \cdot 5H_2O$ [19], although the Cu-

Table 2 Data on structures and thermal decomposition of different aquacopper complexes with heterogeneous coordination sphere

Compound	Structure data		Thermal decomposition			
	$r(Cu–OH_2)$/ Å	$\Delta U_{ii}^{1/2}$/ Å	Decomp. scheme	Decomp. temp./°C	E^*/ kJ·mol^{-1}	lg$A$
$M^I_2[Cu(H_2O)_2](SO_4)_2]$						
M^I =						
NH_4			-2H2O	115	151 ± 5	
Na	1.95		$-2H_2O$	162	276 ± 10	
K	2.01 2.13		$-2H_2O$	127	182 ± 6	
Rb			$-2H_2O$	142	231 ± 12	
Tl			$-2H_2O$	107	146 ± 4	
$[Cu(LL)(H_2O)_2]SO_4$						
LL =						
en	1.975		$-2H_2O$	125		22.6
bipy	1.975		$-2H_2O$	140	161 ± 9	17.0
o-phen	1.970		$-2H_2O$	125	114 ± 6	11.4
$M^I_2[CuCl_4(H_2O)_2]$						
M^I =						
NH_4	1.954	0.054	-2H2O		90 ± 3	
K	1.971	0.035	$-2H_2O$		112 ± 4	
Rb			$-2H_2O$		145 ± 2	
$CuCl_2 \cdot 2H_2O$	1.957	0.013	$-2H_2O$		125 ± 5	

Table 3 Data on structures and thermal decomposition of aquacarboxylatocopper(II) complexes

Compound	Structure data	Thermal decomposition			
	d(Cu–OH$_2$)/ Å	Decomp. scheme	Decomp. temp./°C	E^*/ kJ·mol^{-1}	lg$A$
$Cu(HCOO)_2 \cdot 4H_2O$		$-2H_2O$	20	80 ± 3	8.7
α-$Cu(HCOO)_2(H_2O)_2$	1.974 2.044	$-2H_2O$	54	94 ± 2	21.3
β-$Cu(HCOO)_2(H_2O)_2$		$-0.5H_2O$	22	92 ± 2	12.5
$Cu(HCOO)_2(H_2O)_{1.5}$		$-1.5H_2O$	61	128 ± 2	16.9
$Cu(sal)_2 \cdot 4H_2O$		$-4H_2O$	40	143 ± 3	20.1
$Cu(phthal) \cdot H_2O$	1.961 2.577	$-0.5H_2O$	120	92 ± 8	10.9
$Cu(phthal) \cdot 0.5H_2O$		$-0.5H_2O$	130	144 ± 10	25.3
$Cu(mal) \cdot H_2O$	2.260	$-1H_2O$	90	67 ± 3	5.4
$Cu(citr)_2 \cdot 2H_2O$	2.096 2.284	$-2H_2O$	40	81 ± 2	7.4
$Cu(phenox)_2 \cdot 3H_2O$	2.270 2.020 1.960	$-H_2O$	22	83 ± 3	18.7
$Cu(phenox)_2 \cdot 2H_2O$	1.970 1.990	$-H_2O$	100	80 ± 6	9.8
$Cu(phenox)_2 \cdot H_2O$		$-H_2O$	110	129 ± 7	16.3

Abbreviations: *sal* = $C_6H_4OHCOO^-$, *phthal* = $C_6H_4(COO)_2^{2-}$, *mal* = $C_2H_2(COO)_2^{2-}$
citr = citrate anion $C_2H_4(COO)_2CO(COO)^{4-}$, *phenox* = phenoxyacetate anion $C_6H_5OCH_2COO^-$.

OH_2 distances in the lower hydrates [13, 39, 40] as well as the anisotropic temperature parameters of the donor atoms [39] do not differ so much from those in the $[Cu(H_2O)_4]SO_4 \cdot H_2O$ [13].

Similar relationships were found for dehydration of $M^I_2[Cu(H_2O)_6](SO_4)_2$ and $M^I_2[Cu(H_2O)_2(SO_4)_2]$ [41, 42] (Table 2). The decomposition of hexahydrates starts at far lower temperatures than the decomposition of dihydrates. The sulphato group, being only hydrogen-bonded in hexahydrates, acts in the $Na_2[Cu(H_2O)_2(SO_4)_2]$ as a bidentate bridging ligand, connecting the tetragonal-bipyramidal polyhedra in chains [12]. The elementar cell dimensions were remarkably changed [43] during the dehydration of this compound and new chains formation was assumed. According to the electronic spectra the coordination number 6 was kept, and the IR spectra indicate a further lowering of the SO_4^{2-} symmetry. The changes in the IR and electronic spectra of other $M_2^ICu(SO_4)_2$ compounds are consistent with the coordination number 6 of Cu^{II} atoms and enhanced contacts number of $O(SO_4)$ to the Cu^{II} [44]. The more advantageous positions of uncoordinated oxygen atoms from SO_4^{2-} groups in the structures of already mentioned complexes $[Cu(LL)(H_2O)_2SO_4]$, with *LL* = 2,2'-dipyridine and 1,10-phenanthroline in contrast to the ethylenediamine complex is reflected in the lower activation parameters found for former complexes [38]. The expressive structure changes awaited with the dehydration of the ethylenediamine complex were confirmed by X-ray powder patterns of dehydrated compound [38].

The compound $[Cu(C_6H_5O(CH_2)COO)_2(H_2O)_3]$ is dehydrated in three well resolved steps, in each of them one water molecule is split off [45]. During the first reaction, the phenoxyacetato group, coordinated only through one carboxylic oxygen atom to the Cu^{II} in ther trihydrate [46] form a five-membered pseudo-chelate ring, the kenotic oxygen atom being coordinated to the central atom [47]. This type of coordination may only occur after the rotation of phenoxyacetato group around the Cu–O(carboxyl) bond [46], probably owing to the hydrogen bonds network loosening. The activation parameters (Table 3) are low, reflecting the small changes in the packing of the molecules in the elementar cell [47]. Further dehydration stops at monohydrated compound, which crystal structure is not known. The electronic spectra of the different hydrates confirmed changes in coordination polyhedra symmetry. The IR spectra of the compounds exhibit differences only in the region 1100–1150 cm^{-1} in which C–O–C vibrations are active. Absorption bands, corresponding to the water molecules vibrations found for tri- and dihydrates at 3575 cm^{-1} disappear after monohydrate formation and only an absorption band of low intensity at 3170 cm^{-1} was found in the IR spectrum of this compound [45].

Although both complexes $[Cu(C_6H_4(COO)_2)(H_2O)]$ and $[Cu(C_2H_2(COO)_2)(H_2O)]$ do contain one coordinated water molecule they exhibit considerable differences in bonding mode of the anions and water molecule [48, 49] and consequently quite different course of dehydration was observed:

$$[Cu(C_6H_4(COO)_2)(H_2O)] \rightarrow [Cu(C_6H_4(COO)_2)(H_2O)]_2$$

$$\rightarrow [Cu(C_6H_4(COO)_2)]$$

$$[Cu(C_2H_2(COO)_2)(H_2O)] \rightarrow [Cu(C_2H_2(COO)_2)]$$

Table 4 Data on structures and thermal decomposition of pentacoordinate aquacopper(II) complexes with chelate ligands

Compound	Structure data		Thermal decomposition			
	d(Cu–OH$_2$)/ Å	$\Delta U_{ii}^{1/2}$/ Å	Decomp. scheme	Decomp. temp./°C	E^*/ kJ·mol^{-1}	lg$A$
[Cu(en)$_2$(H$_2$O)]X$_2$						
X^- =						
Cl	2.620		–H$_2$O		132 ± 6	
Br	2.780		–H$_2$O		156 ± 6	
[Cu$_2$(CN)$_4$]$^{2-}$	2.441		–H$_2$O	115	75 ± 7	
[Cu$_2$(SeCN)(CN)$_3$]$^{2-}$	2.331		–H$_2$O	105	83*	
[Ni(edta)]	2.632		–H$_2$O	70	48 ± 4	
[Cu(bipy)$_2$(H$_2$O)]·S$_2$O$_6$	2.158	0.036	–H$_2$O	135	76 ± 10	
[Cu(o-phen)$_2$(H$_2$O)]·(BF$_4$)$_2$	2.235	0.022	–H$_2$O	51	83 ± 2	
[Cu(o-phen)$_2$ (H$_2$O)]·(NO$_3$)$_2$	2.183	0.026	–H$_2$O	102	166 ± 12	

Abbreviations: *en* = ethylenediamine; *bipy* = 2,2'–dipyridine; *o–phen* = 1,10–phenanthroline, *edta* = ethylenediaminetetraacetato tetraanion

The formation of hemihydrated and anhydrous compound in the upper reaction is connected with only small crystal structure changes. As indicated by the electronic spectra [26] in the hemihydrate are present dimeric units Cu–OH$_2$–Cu and the other emptied coordination sites are occupied by initially free carboxylic oxygen atoms, the coordination number 6 being retained. The coordination of free oxygen atoms continues also in the second dehydration step. The dehydration of copper(II) maleinate monohydrate is also accompanied by only slight changes of the crystal structure, however the electronic spectra indicate that the Cu^{II} coordination polyhedra are square-planar after dehydration [45]. This is in accordance with the bonding mode of maleinate anions in the reactant – each of them is coordinated to three different copper atoms, with one of them a seven-membered metallocyclus is formed. The extended and rigid bonding of the anion to the central atom in the equatorial plane and only loose interaction of the central atom with the water molecule in the apical position of a tetragonal pyramid are the most important factors influencing the formation of square-planar structure of the coordination polyhedra in the dehydrated compound. Dehydration of several further complexes with such a 'rigid' structure of the anionic part of coordination compounds, or with anions which are not capable to form more contacts to the central atom was studied as well. Rigid anionic framework as [Cu$_2$(CN)$_4$]$^{2-}$ or [Cu$_2$(SeCN)(CN)$_3$]$^{2-}$ occurs with complex cation $[Cu(NH_2CH_2CH_2NH_2)_2(H_2O)]^{2+}$ [50, 51]. Dehydration of square-pyramidal $[Cu(en)_2(H_2O)]^{2+}$ cation leads again to a square-planar cation and low values of E^* were found [24] for the reaction. With the dehydration of trigonal-bipyramidal complexes $[Cu(phen)_2(H_2O)]X_2$ (*phen* = 1, 10 phenanthroline, X^- = BF_4, NO_3) [52, 53] a tetrahedral deformation of remaining complex cation took place with anion BF_4^-, but the coordination of NO_3^- was observed [24]. Different energetical needs for occurring structure changes were also reflected in E^* and ΔH values, both being smaller for the former complex (Table 4). Dehydration of the compounds $M_2^I[CuCl_4(H_2O)_2]$, where M were NH_4, K and Rb and that of $CuCl_2 \cdot 2H_2O$ takes place in one step [54]. The established values of E^* and lg$A$ (Table 2) are generally lower than those found for other dihydrate compounds. This finding is in accordance with the fact that no expressive changes in the structure of the remainder are to be awaited, because of the bridge-bonding of the chloroligands in the reactants [55, 56]. However, there is a possibility of tetrahedral deformation of originally square-planar Cu^{II} coordination polyhedra, indicated also by thermal dependence of the vibrational modes responsible for this change [57]. Finally, we would like to underline that activation parameters, found for these reactions do not follow the changes in the Cu–OH_2 bond distances either. The values of activation parameters for the dehydration of these complexes were found to be the higher, the lower the value of $\Delta U_{ii}^{1/2}$ was [54]. The same dependency of the E^* values for dehydration of $[Cu(LL)(H_2O)]X$ (LL = 2,2'-dipyridine, $X = S_2O_6^{2-}$ [57], LL = 1,10-phenanthroline, $X = 2BF_4^-$ [58]) on the $\Delta U_{ii}^{1/2}$ values was established [24].

Conclusions

On the basis of the results discussed in this paper one can draw the following conclusions:

1. The reaction pathway of the hexaquacopper(II) complex dehydration is indicated by the fluxionality or rigidity of the $[Cu(H_2O)_6]^{2+}$ cation. Fluxional cations, having at room temperature rhombically distorted elongated tetragonal bipyramida coordination polyhedra undergo heating symmetry change to a compressed tetragonal bipyramidal and all four longer Cu–H_2O bonds are split in the first reaction step. Rigid cations $[Cu(H_2O)_6]^{2+}$ exhibit at room temperature elongated tetragonal bipyramidal structures, which do not change at elevated temperatures and only two water molecules are evolved in the first dehydration step.

2. The hydrogen bonds network breakdown or its loosening due to crystal and/or coordinated water molecules escape can lead to a rearrangement of the

remaining chemical bonds. This supports our ideas that the quantitative (kinetic and thermodynamic) parameters gained from thermoanalytical measurements do not have to be correlated to the lengths of the broken bonds only. The kinetic parameters (E^* and lg$A$ values) of the dehydration depend rather on the structural presumptions of the reactant to form a lower hydrate.

3. Out of the room temperature monocrystal structure data on the dehydrated compounds the anisotropic temperature parameters of donor atoms, corrected for the thermal movement of the central atom ($\Delta U_{ii}^{1/2}$ values) in the bond direction are the most indicative for the reaction pathway. Also the activation energy values found for these reactions are in the best correlation with these structure parameters: the higher the $\Delta U_{ii}^{1/2}$ values for the broken bonds are, the lower the experimental E^* values are.

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Zusammenfassung — Hinsichtlich des Aspektes von strukturellen Veränderungen, die beim Erhitzen bis zur Zersetzungstemperatur und während der Dehydratation ablaufen, wurden die Dehydratationsstufen von Aquakupfer(II)-komplexen mit homogener und heterogener Koordinationssphäre untersucht. Die Bedeutung des Verlustes von intra- und intermolekularen Wasserstoffbrückenbindungen in der Zersetzungsreaktion für die Strukturveränderungen des Restes und die Strukturvermutungen für die Reaktanden für die Bildung niedriger Hydrate wird diskutiert.

Man fand, daß die Aktivierungsparameter der Dehydratation um so niedriger sind, je geringer der Strukturunterschied zwischen Reaktand und Produkt. Sie spiegeln weniger die Bindungslänge zwischen Zentralatom und flüchtigem Ligand, als eher die Gesamtstrukturunterschiede zwischen Ausgangsmaterial und Produkt wieder. Von allen Daten der Kristall- und Molekularstruktur der dehydratierten Verbindungen wird der Reaktionsweg am besten durch Anisotropietemperaturparameter des Donoratoms, korrigiert um die thermische Bewegung des Zentralatomes, angezeigt: je größer diese Werte in der Bindungsrichtung sind, um so kleiner sind die Werte der Aktivierungsenergien der Dehydratation.