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

XII. Are there only the split - off bonds activated during dehydration of copper carboxylates?

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The study of the thermal dehydration of the compounds $CuX_2.nH_2O$, where X^- were formate, salicylate or phtalate anions, was performed, including the observations of structural changes of compounds during their decomposition. It is shown that the dehydration of copper(II) formate tetra- and dihydrates is accompanied by significant changes in the bonding of the formato groups and remaining water molecules. Two structurally different modifications of $Cu(HCOO)_2.2H_2O$ were prepared, the structure differences are clearly demonstrated in their decomposition stoichiometry. The dehydration of copper formate hydrates was found to be controlled by chemical reaction on the phase boundary. The dehydration of the copper salicylate tetrahydrate and copper phtalate monohydrate is accompanied by the structural changes of the whole compounds, as well, however these processes are diffusion or nucleation controlled.

Thermal decomposition reactions of coordination compounds are in the fact ligand substitution reactions in the solid state, the leaving ligand being substituted by originally outer shell anions or molecules. Another possibility is that the ligands, not released in the reaction, enhance the number of formed coordination bonds. Such processes need in many cases the reconstruction of the whole network of the chemical bonds and the course of the decomposition reactions is dependent on the overall structures of the coordination compounds [1, 2].

The dehydration of several Cu(II) aquacomplexes with heterogeneous coordination spheres, as occur in some hydrates of copper(II) carboxylates was widely studied and compared with the same reactions of other central

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atoms carboxylates [3-7]. The study of mutually isomorphous compounds $M(HCOO)_2.2H_2O$, where M stands for divalent atoms of the first transition row [3] showed that the lowest thermal stability, measured as the starting temperature of the decomposition and it's activation energy, can be attributed to the Cu(II) compound. Because these data were related to the bond strength of the $M-OH_2$ bonds [3], we collected the known crystal structure data on these compounds. As it can be seen (Table 1), although the correlations between the $M-OH_2$ distances and decomposition temperatures and activation energies hold for other studied central atoms, they fail for the $Cu(HCOO)_2.2H_2O$. We think that the bond distances central atom - leaving ligands would be the dominant factors only in the cases when no other changes in the compound's structure would take place. The dehydration of several divalent transition metals salicylates was studied, as well [6]. However, the established array of their thermal stability was different from that found for analogous formates.

Table 1 The data on the thermal dehydration of compounds $M(HCOO)_2.2H_2O$ [3] in comparison with the bond distances $M-OH_2$

M(II)		E^*, kJ mol^{-1}	$r(M-OH_2)$, pm		Ref.
Mn	d^5	106.8	221.6	216.8	8
Fe	d^6	108.4	208.4	215.3	9
Co	d^7	111.8	206	207	10
Ni	d^8	117.5	204.2	205.9	11
Cu	d^9	103.2	197.4	204.4	12
Zn	d^{10}	102.4	210.3	205.0	13

In this contribution we want to demonstrate that the heating of the compounds leads to the activation of the whole chemical bonds network, which may be reflected in the completely changed structural situation in the product. This was the aim of the present study of the thermal dehydration of the hydrated copper formate, salicylate and phtalate.

Experimental

Chemicals: $CuSO_4.5H_2O$ p. a., $NH_{3(aq)}$ p. a., $C_6H_4OHCOONa$ p. a., $C_6H_4(COOH)_2$ p. a.

Syntheses: The investigated complexes were prepared according to the known methods: $Cu(HCOO)_2.4H_2O$ [15], β-$Cu(HCOO)_2.2H_2O$ [4],

$Cu(C_6H_4OHCOO)_2.4H_2O$ [16], $Cu(C_6H_4OHCOO)_2.2H_2O$ [17] and $Cu\{C_6H_4(COO)_2\}.H_2O$ [18]. All other compounds were prepared via regulated thermal decomposition of the listed ones.

Analytical methods: Copper(II) content in the prepared compounds was determined complexometrically against murexide indicator. The water content was ascertained from the thermal decomposition curves. The elemental analysis gave the carbon and hydrogen contents. The analytical compositions of the studied compounds are shown in the Table 2.

Table 2 Chemical analysis of the prepared compounds

Compound	% Cu		% C		% H		% H_2O	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
$Cu(HCOO)_2.4H_2O$	28.16	28.20	10.64	10.38	4.48	4.80	31.94	31.58
α-$Cu(HCOO)_2.2H_2O$	33.51	33.56	12.66	12.44	3.19	3.06	19.00	18.80
β-$Cu(HCOO)_2.2H_2O$	33.51	33.52	12.66	12.71	3.19	3.22	19.00	18.50
α-$Cu(HCOO)_2$	41.37	41.40	15.62	15.50	1.31	1.41		
β-$Cu(HCOO)_2$	41.37	41.29	15.62	15.70	1.31	1.39		
$Cu(sal)_2.4H_2O$[a]	15.50	15.59	40.99	41.25	4.43	4.50	17.00	17.50
$Cu(phtal).H_2O$[b]	25.86	25.50	39.08	39.10	3.28	3.31	7.33	7.20
$Cu(phtal).0.5H_2O$	26.85	26.84	38.95	38.90	2.98	2.94	3.80	3.50
$Cu(phtal)$	27.91	27.90	42.17	42.08	1.77	1.80		

[a] salicylate anion $C_6H_4OHCOO^-$

[b] phtalate anion $C_6H_4(COO)_2^{2-}$

Apparatus: The thermal decomposition of the compounds was studied with an OD 102 derivatograph (MOM Budapest). Ceramic crucibles with an upper diameter of 14 mm were used. The temperature was measured with Pt, Pt-Rh thermocouple. The sample weight was 200 mg, the temperature increase was 2.5 deg min^{-1}. X-ray powder patterns of the compounds were gained on the Czechoslovak goniometer GON - 2 with CuK_α radiation and Ni filter.

Infrared spectra were taken on Specord 75 - IR spectrophotometer in the region 400 - 1700 cm^{-1}, the electronic spectra were measured on Specord M - 40 between 11.000 and 35.000 cm^{-1} or Unicam SP 700 (7.000 - 18.000 cm^{-1}) was used. Both types of measurements were done using nujol suspension technique. In some cases magnetic moments at room temperature were measured, using Guy method and $CuSO_4.5H_2O$ as standard. Diamagnetic corrections have been computed by means of Pascal's constants. The values of effective magnetic moments were calculated according to the equation

$\mu_{eff} = X'_M T$.

The specific surface of samples, sieved to various mesh sizes were measured using the B.E.T. method on Sartorius thermobalances. Measurements of the thermal properties of studied compounds and the evaluation of kinetic parameters.

All samples, before measurements, were finely powdered and sieved to a mesh size of 0.18. Activation parameters for the studied reactions were evaluated from the TG curves using the Coats - Redfern [14] and Škvára-Šesták [19] methods. For the method [14] least squares procedure was used, the reaction order *n* was choosen from 5 values (0, 1/3, 1/2, 2/3 and 1) according to the criterion of the best linearity.

Results and discussion

Two well defined hydrates of copper formate are known - the tetra- and dihydrate. In the compound $Cu(HCOO)_2.4H_2O$, there are only two water molecules coordinated to the central atom, remaining two being placed between copper formate sheets together with both coordinated water molecules [20]. Under experimental conditions, used in this work, the tetrahydrate decomposes in the first step into the dihydrate (Fig. 1). According to the X-ray (Fig. 2) powder patterns, the last compound has the same crystal structure as it was found for crystalline $Cu(HCOO)_2.2H_2O$ in [12]. This crystal structure consists from two types of coordination polyhedra. The first of them is formed by oxygen atoms from six different formato groups, the other by four water molecules, placed in the equatorial plane and two oxygen atoms from bridging formate groups in the axial positions. Considering the structures of both compounds, we have to assume serious changes in the network of the chemical bonds. Because the formato groups have in the reactant anti - anti [20] and in the product anti - syn (one half) or anti - anti (the second half) configuration [12] it is obvious that in the studied reaction are not involved only the originally uncoordinated water molecules, but at least one half of the chemical bonds Cu - OH_2 and Cu - O (formate) should be reconstructed. According to the X-ray powder patterns of the decomposition intermediates (Table 3) the tetrahydrate is in the reaction mixture present even after lost of more that 1 mole H_2O per 1 mole of complex, the dihydrate appears in the reaction mixture at the very beginning of the decomposition. However, the powder diffractograms of the dehydration intermediates couldn't be completely indexed when considering

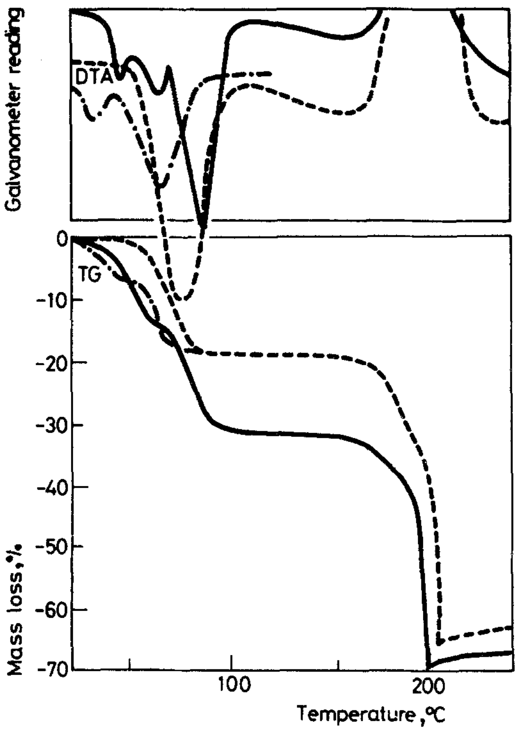

Fig. 1 Thermal decomposition of the copper formate hydrates: $Cu(HCOO)_2.4H_2O$ (——), α-$Cu(HCOO)_2.2H_2O$ (– – –) and β-$Cu(HCOO)_2.2H_2O$ (– · – · –)

the presence of both hydrates, nor when considering the presence of the "royal blue" $Cu(HCOO)_2$, which is the only product of decomposition of the $Cu(HCOO)_2.4H_2O$ in vacuo [5]. It can be therefore assumed that during the dehydration a new phase is formed, which couldn't be identified till now.

When preparing the $Cu(HCOO)_2.2H_2O$ according to [4] from a solution, the gained product differed from that obtained through dehydration of $Cu(HCOO)_2.4H_2O$ in its powder pattern (Fig. 3) and infrared spectrum (Fig. 4). The compound, labelled as β-$Cu(HCOO)_2.2H_2O$ is thermodynamically less stable than the product of the thermal dehydration of $Cu(HCOO)_2.4H_2O$, labelled as α-form. The greenish-blue β-form changes into the light blue α-$Cu(HCOO)_2.2H_2O$ in few days at the room temperature. The differences in the powder patterns of the both compounds (Figs 2 and 3) indicate different interplanar distances and different occupation of the diffraction planes. On the basis of the IR spectra of both compounds

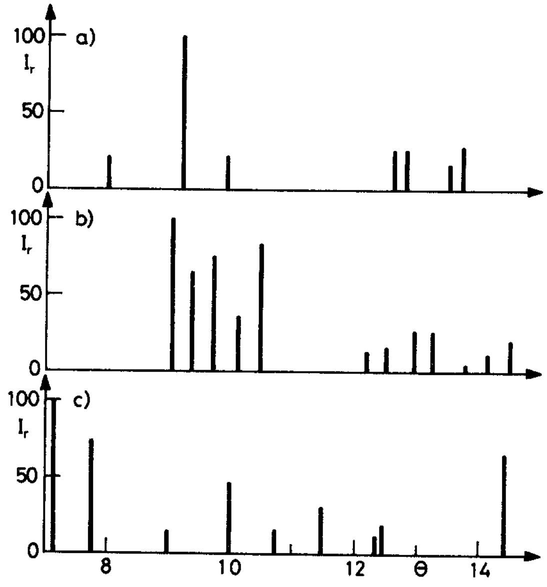

Fig. 2 The X-ray powder patterns of a. α-$Cu(HCOO)_2$, b. α-$Cu(HCOO)_2.2H_2O$ and c. $Cu(HCOO)_2.4H_2O$

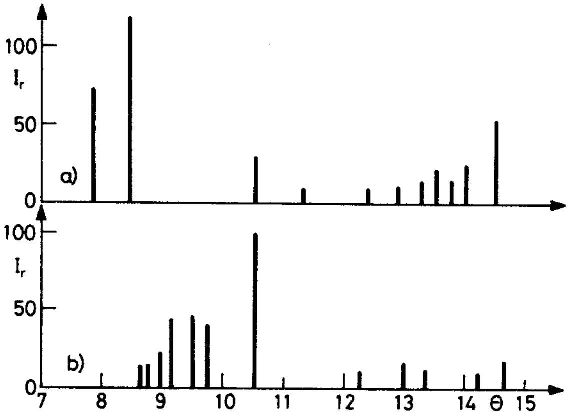

Fig. 3 The X-ray powder patterns of a. β-$Cu(HCOO)_2$, b. β--$Cu(HCOO)_2.2H_2O$

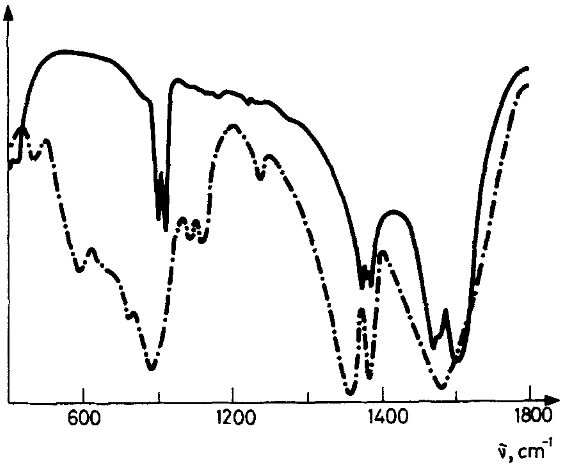

Fig. 4 The IR spectra of the α-$Cu(HCOO)_2.2H_2O$ (——) and β--$Cu(HCOO)_2.2H_2O$ (–·–·–)

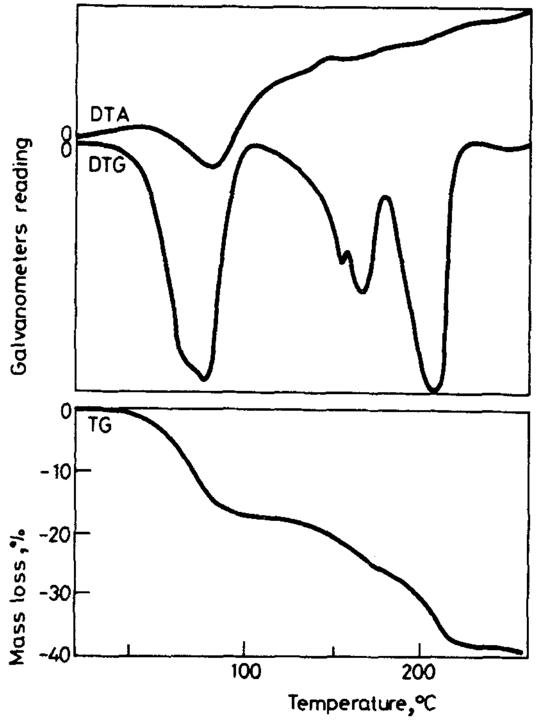

Fig. 5 The thermal decomposition of the $Cu(sal)_2.4H_2O$

Table 3 The X-ray powder patterns of the intermediates of the dehydration of the $Cu(HCOO)_2.4H_2O$

$Cu(HCOO)_2.3.7H_2O$			$Cu(HCOO)_2.2.96H_2O$			$Cu(HCOO)_2.2.5H_2O$		
2Θ	I_r, %		2Θ	I_r, %		2Θ	I_r, %	
14.2	86	T	14.4	43	T			
14.65	25							
15.45	100	T	15.4	17	T			
17.0	28		17.0	32		17.0		
18.0	100	T,D	18.0	90	T,D	18.0	98	T,D
18.95	67	T,D	18.95	81	T,D	18.70	77	T,D
19.40	91	T,D	19.40	80	T,D	19.40	87	T,D
21.00	65	D	21.0	100	D	21.0	100	D
27.3	46	T						
22.6	42	T						
24.1	21	T						
24.4	38	T,D	24.4	23	T,D	24.3	23	T,D
						24.9	22	T,D
			25.1	22	D			
26.0	18	D	26.0	34	D	26.0	44	D
26.7	30	D	26.7	35	D	26.7	40	D

Abbreviations T: $Cu(HCOO)_2.4H_2O$, D: α-$Cu(HCOO)_2.2H_2O$

(Fig. 4) different coordination of formato groups to the central atom can be suggested, because the most pronounced differences were found for ν_1 (CO) vibration in the region 1320-1380 cm^{-1}, which is especially sensitive to the mode of $HCOO^-$ coordination [21]. The coordination polyhedra of Cu(II) are in both compounds nearly equally deformed $\tilde{\nu}_{max}$ (d-d) being 12.900 cm^{-1} for the α-form and 12.800 cm^{-1} for the β-form, respectively.

The dehydration of the copper formate hydrates was studied from the view point of its stoichiometry and kinetics. The data on the decomposition temperatures and stoichiometries are given below:

$$Cu(HCOO)_2.4H_2O \xrightarrow{20^{o}} \alpha\text{-}Cu(HCOO)_2(H_2O)_2 \qquad (1)$$

$$\alpha\text{-}Cu(HCOO)_2(H_2O)_2 \xrightarrow{54^{o}} \alpha\text{-}Cu(HCOO)_2 \qquad (2)$$

$$\mu_{eff} = 1.99 \text{ B.M.} \qquad \mu_{eff} = 1.96 \text{ B.M.}$$

$$\beta\text{-Cu(HCOO)}_2.2H_2O \xrightarrow{22^o} \text{Cu(HCOO)}_2.1.5H_2O \qquad (3)$$

$$\mu_{eff} = 1.96\ \text{B.M.} \qquad \mu_{eff} = 1.93\ \text{B.M.}$$

$$\text{Cu(HCOO)}_2.1.5H_2O \xrightarrow{61^o} \beta\text{-Cu(HCOO)}_2 \qquad (4)$$

$$\mu_{eff} = 1.72\ \text{B.M.}$$

The structural differences between both forms of $Cu(HCOO)_2.2H_2O$ are reflected in their decomposition stoichiometry (Fig. 1) as well as in the structures of the reaction products. The influence of the preparation mode of the copper formate dihydrates on the stoichiometries of their thermal decomposition is mentioned in [4], as well, but without consideration of the possible structure differences between them. Although the composition of the product of the reaction (3) would suggest a dimeric structure, the electronic spectrum of this compound and it's room temperature magnetic moment do not allow to consider the copper acetate type structure.

From the literature, three modifications of the anhydrous copper formate are known, but only the crystal structure of the α-$Cu(HCOO)_2$ (the royal blue modification) is known [22]. In this compound is the Cu(II) pentacoordinated, all $HCOO^-$ have anti-syn configuration. Therefore, during the dehydration of the α-$Cu(HCOO)_2(H_2O)_2$ the bonds Cu-O (formate) have to be activated and reconstructed, too.

The kinetic evaluation of the studied dehydration reactions of the copper(II) formate hydrates (Table 4) showed that the reactions are controlled by the chemical reaction on the phase boundary. The influence of the particle's size on the activation parameters was studied for $Cu(HCOO)_2.4H_2O$ (Table 5). According to these results, the activation parameters are not influenced by the size of the decomposed particles. The values of activation energies and preexponential factors, established for the dehydration of the Cu(II) formate hydrates are relatively low (Table 4). Although the activation energies, found for the first decomposition step of the α- and β-$Cu(HCOO)_2.2H_2O$ are quite near to each other, the values of the preexponential factors are considerably different. This would mean that the reactions are entropy controlled and the structure changes, accompanying the dehydration are different for the both forms of $Cu(HCOO)_2.2H_2O$. These findings are in good correlation with the results given above.

Table 4 The results of kinetic analysis of the dehydration of the studied compounds

Compound	Coats- Redfern			Škvára- Šesták		
	E^*, kJ mol^{-1}	log$A$	n	E*, kJ mol^{-1}	log$A$	Mechanism
Cu(HCOO)$_2$.4H$_2$O	79.6±2.5	8.7	2/3	69.5±1.6	8.7	R3
α-Cu(HCOO)$_2$.2H$_2$O	93.9±2.1	21.3	2/3	104.0±3.5	21.0	R3
β-Cu(HCOO)$_2$.2H$_2$O	91.8±1.6	12.5	2/3	95.0±4.2	13.1	R3
Cu(HCOO)$_2$.1.5H$_2$O	128.0±2.0	16.9	2/3	123.4±5.5	15.8	R3
Cu(sal)$_2$.4H$_2$O	142.7±3.2	20.1	1	160.5±8.8	20.6	D3
Cu(phtal).H$_2$O	92.0±8.0	10.9	1	131.0±10.0	12.3	D3
Cu(phtal).0.5H$_2$O	144.0±9.5	25.3	2/3	142.0±11.5	21.9	A4

R3: $g(\alpha) = [1-(1-\alpha)^{1/3}]^{1/3}$; D3; $g(\alpha) = [(1+\alpha)1/2 - 1]^2$; A4: $g(\alpha) = [-\ln(1-\alpha)^{3/4}]$

Table 5 The size of decomposed particles of the $Cu(HCOO)_2.4H_2O$ and the activation energy of the dehydration

Fraction size,	Specific surface, of pores	Mean radius	E^*,	n	E^*,	Mechanism
mm	m^2/g	μm	$kJ\ mol^{-1}$[14]		$kJ\ mol^{-1}$[19]	
0.40-0.18	4.47	3.81	77.3±3.8	2/3	73.5±1.7	R3
0.18-0.15	4.74	3.80	79.6±2.5	2/3	69.4±2.1	R3

The copper(II) salicylate is known in tetrahydrated, dihydrated and anhydrous forms. In the tetrahydrate, there are two water molecules coordinated to the Cu(II), the next two are in the crystal structure hold by an extended system of hydrogen bonds [16]. The structure of the copper(II) salicylate dihydrate is of OD type, copper(II) atom being pentacoordinated [17]. Although the structure and bonding situation in the $Cu(sal)_2.4H_2O$ seems to be analogous with the copper(II) formate tetrahydrate, the course

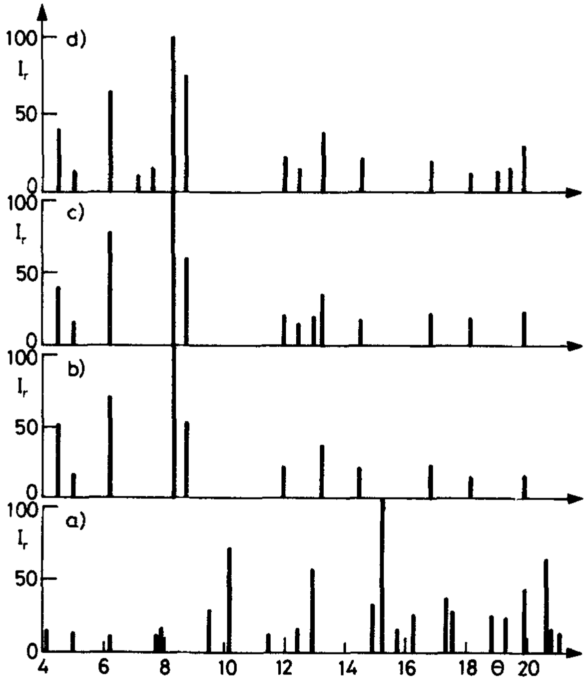

Fig. 6 The X-ray powder patterns of the a. $Cu(sal)_2.4H_2O$, b. $Cu(sal)_2.3.37H_2O$, c. $Cu(sal)_2.2.5H_2O$ and $Cu(sal)_2.2H_2O$

of its thermal decomposition is quite different. To the contrary with the literature data [16], the heating of this compound leads to its anhydrous form (Fig. 5), the release of the last portions of water is connected with the partial decomposition of the compound. This reaction stoichiometry is probably due to the overall lowering of the crystal stability, caused by the break-down of the original hydrogen bonds network. The compound Cu(sal).$2H_2O$ can be prepared from the tetrahydrate by a slow dehydration at the room temperature. The powder diffractograms of the partially decomposed $Cu(sal)_2.4H_2O$ (Fig. 6) show the complete absence of the tetrahydrate at the ratio H_2O : Cu(II) = 3.37 : 1, which is completely different picture than observed for the dehydration of the $Cu(HCOO)_2.4H_2O$.

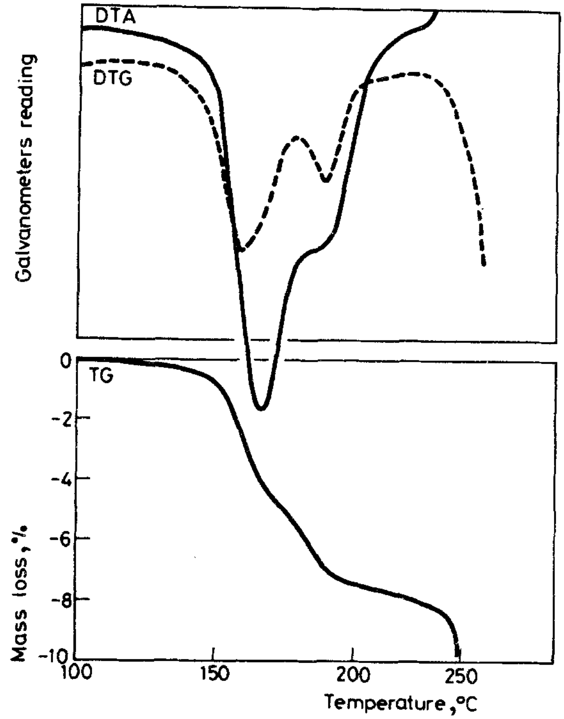

Fig. 7 The thermal decomposition of the Cu(phtal).H_2O

According to the kinetic data (Table 4) is the reaction rate diffusion controlled. The activation parameters found for the dehydration of the

$Cu(sal)_2.4H_2O$ are markedly higher than those found for copper(II) formate tetrahydrate.

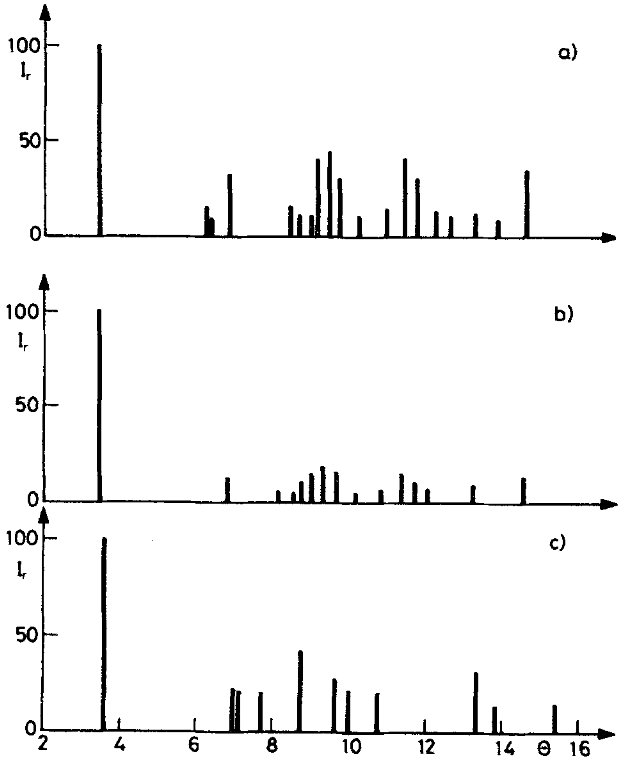

Fig. 8 The X-ray powder patterns of the a. $Cu(phtal).H_2O$, b. $Cu(phtal)_2.0.5H_2O$ and c. Cu(phtal)

Hexacoordinated atom Cu(II) occurs in the compound Cu(phtalate).H_2O, where the water molecules and phtalate groups form bridges between two crystallographically unequivalent Cu(II) atoms [18]. The decomposition stoichiometry (Fig. 7), found at isothermal [7] conditions, as well as at dynamic conditions, used in this work is the same. The intermediate of the decomposition - Cu(phtalate).$0.5H_2O$ - is according to it's X-ray powder patterns (Fig. 8) and electronic spectra a new individuum. Although the powder patterns of Cu(phtalate) monohydrate, hemihydrate and of anhydrate are very similar, indicating only slight changes in the crystal structures, the electronic spectra of them indicate substantial changes in the symmetries of the coordination polyhedra in the first decomposition step. In the electronic spectrum of the Cu(phtalate). H_2O there is an absorption maximum, corresponding to the d-d transitions, centered at 14.800 cm^{-1} with an intense shoulder at ~12.500 cm^{-1}. The energetically higher absorption band was preserved in the electronic spectrum of the hemihydrates as well, but the low-energy shoulder was shifted to the 11.900 cm^{-1}. More over a new band appeared in the spectrum, centered at ~26.500 cm^{-1}. This may indicate the presence of the units $[Cu_2(H_2O)]^{4+}$, which absorb at these wavelengths, according to [23]. The anhydrous copper(II) phtalate exhibits absorption bands at 25.000, 14.700 and 11.900 cm^{-1}, the low energy shoulder being more intensive than at hemihydrate. The results of the X-ray powder analysis and electronic spectra of all three compounds show that although the changes in the crystal structures of the compounds are not that expressive as found for formates and salicylates, they are accompanied by marked changes in the symmetries of coordination polyhedra. This would mean that again other, not only the broken chemical bonds should be activated during the heating. However, in this case as well as at the dehydration of the $Cu(sal)_2.4H_2O$ we can not be sure whether these bonds are released and newly formed during the process or not.

The kinetic evaluation of both the decomposition reactions of the Cu(phtalate).H_2O gave results, indicating that the diffusion (the first decomposition step) or nucleation (the second step) are the rate controlling mechanism, respectively (Table 4). The value of the activation energy for the formation of the hemihydrate is in good agreement with the data [7], we have found lower activation energy for the second decomposition step as in [7] (Table 4).

Concluding we can say that the studied dehydration reactions are connected with more or less expressive changes in the crystal structures, symmetries of coordination polyhedra and binding modes of the nonvolatile ligands. Consequently all chemical bonds, present in the decomposed compound are activated during the process and the decomposition stoichiometry as well as the activation parameters depend on the structure of the whole compound and can not be correlated with the strength or other characteristics of the split bonds only.

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Zusammenfassung — Es wurde die thermische Dehydratation der Verbindungen $CuX_2.nH_2O$ mit dem Formiat-, Salicylat- und Phthalatanion als X^- unter gleichzeitiger Beobachtung eventueller Strukturveränderungen dieser Verbindungen während der Dehydratation untersucht. Es wird gezeigt, dass die Dehydratation von Kupfer(II)-formiat Tetra- bzw. Dihydrat von einer eindeutigen Veränderung der Bindungsverhältnisse der Formiatgruppen und der verbleibenden Wassermoleküle begleitet wird. Es wurden zwei strukturell verschiedene Modifikationen von $Cu(HCOO)_2.2H_2O$ hergestellt, die Strukturunterschiede zeigen sich deutlich in der Stöchiometrie ihrer Zersetzung. Die Dehydratation von Kupferformiathydraten wird durch die chemische Reaktion an der Phasengrenze kontrolliert. Die Dehydratation von Kupfersalicylat Tetrahydrat und Kupferphthalat Monohydrat wird von einer Strukturveränderung des ganzen Moleküles begleitet, unabhängig davon, ob der Vorgang durch die Diffusion oder Kernbildung bestimmt wird.