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

XI.Stoichiometry and kinetics of dehydration of the compounds $M_2^I[M^{II}(H_2O)_6](SeO_4)_2$

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The thermal dehydration of the compounds $M_2^I[M^{II}(H_2O)_6](SeO_4)_2$, where M^I = NH_4, K, Rb, Cs and Tl, and M^{II} = Cu and Ni, was studied in order to correlate the course of the decomposition with the known crystal structures. It was found that the stoichiometry of the reactions is the same as that established for the analogous sulphato compounds of Cu(II) and Ni(II), respectively. Because of the discrepancies between the room-temperature crystal structures and the observed decomposition stoichiometries, high-temperature powder diffractograms were taken. These indicated structural changes of the copper(II) compounds during heating. The powder patterns for different structure changes were calculated and compared with the experimental ones. It was shown that during the heating two axial Cu-H_2O bonds are shortened and two equatorial bonds are lengthened. The observed decomposition stoichiometry is compatible with the formation of four nearly equal Cu-H_2O bonds. The activation energies (E*) and pre-exponential factors (log A) for the first dehydration reaction of the Cu(II) compounds display the following sequence of M^I: Tl > Rb > NH_4 > K, and they are the higher, the shorter the split equatorial Cu(II) bonds. For the compounds of Ni(II) the sequence of E* and log A values is K > Tl > NH_4 > Rb > Cs.

It was shown previously [1, 2] that the symmetry of the Cu(II) coordination polyhedron is one of the important factors influencing the stoichiometry and the kinetics of the thermal decomposition of coordination compounds with Cu(II) as central atom. The fact that compounds with rhombically deformed coordination polyhedra, such as $M_2^I[Cu(H_2O)_6](SO_4)_2$, exhibit decomposition stoichiometry which would correspond better to tetragonal

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symmetry has not yet been explained. We presume that these "discrepancies" between the course of thermal decomposition and the Cu(II) coordination polyhedra structures are observed because the room-temperature structures are correlated with the course of reactions that usually take place at higher temperatures. It is known that the structures of the plastic Cu(II) coordination polyhedra [3] are very sensitive to external influences (temperature, pressure, counter-ions). The heating of many compounds, e.g. $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ [4] or $K_2Pb[Cu(NO_2)_6]$ [5], from liquid nitrogen temperature to room-temperature leads to changes in the Cu-ligand bond distances, resulting in the formation of dynamic octahedral Cu(II) coordination polyhedra [4, 5].

In this work we have tried to identify the structural changes occurring in the compounds $M^I_2[Cu(H_2O)_6](SeO_4)_2$ during heating, using powder diffractograms taken at room-temperature and at temperatures only slightly lower than the decomposition temperatures. The goal of these attempts was to establish whether it is possible to correlate the structural changes caused by high temperature with the course (stoichiometry and kinetics) of the dehydration of these compounds, as found for the decomposition of the compounds $M^I_2Pb[Cu(NO_2)_6]$ [6].

Experimental

Chemicals: $CuSO_4.5H_2O$, CuO, $NiCl_2.6H_2O$, KOH, $Ba(OH)_2.8H_2O$, NH_3(aq), H_2O_2(aq, 30%) all p.a. grade, LaChema, Brno; Rb_2SO_4, Cs_2SO_4, Tl_2SO_4 p.a. grade, Serva Int. Chemie u. Handels GmbH; H_2SeO_3, pure Reachim, USSR.

Synthesis: The compounds $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$ were prepared by crystallization form aqueous solutions containing $M^I_2SeO_4$ and $M^{II}SeO_4$ in a molar ratio of 1:1 with a small excess of H_2SeO_4 to prevent hydrolysis. Selenic acid was prepared form H_2SeO_3 according to [7]. The solutions of $M^{II}SeO_4$ were prepared by dissolving CuO or $Ni(OH)_2.nH_2O$ in H_2SeO_4 solution. The $M^I_2SeO_4$ crystallized from the solutions gained by neutralization of the selenic acid with a solution of the appropriate base. These solutions were prepared by reaction of the parent sulphates with barium hydroxide solution.

Analytical methods. The content of M^{II} in the prepared compounds was determined complexometrically, and the water content was established from the thermogravimetric curves. The results are given in Table 1, together with the analytical data on the decomposition intermediates.

Table 1 Analytical data on the compounds $M^I_2[M^{II}(H_2O)_n](SeO_4)_2$

M^{II}	M^I	n	% M^{II}		% H_2O	
			calc	found	calc	found
Cu	NH_4	6	12.87	12.89	21.90	21.6
		2	15.07	14.89	8.55	7.8
	K	6	11.86	11.94	20.18	19.8
		2	13.70	13.81	7.77	7.1
	Rb	6	10.11	10.16	17.20	17.2
		2	11.42	11.67	5.73	6.6
	Cs	6	8.78	8.82	14.94	14.9
	Tl	6	7.33	7.34	12.48	12.4
		2	8.00	8.25	4.16	4.5
Ni	NH_4	6	12.01	11.90	22.11	21.3
	K	6	11.06	11.10	20.36	20.7
		2	12.79	12.23	7.85	8.4
	Rb	6	9.41	9.72	17.33	17.2
	Cs	6	8.17	8.24	15.04	14.8
	Tl	6	6.81	6.95	12.55	12.7

*Apparatus and measuring conditions.*The powder diffractograms of the studied complexes were produced on a GON-2 goniometer (Czechoslovakia) with CuK_α radiation and a Ni filter. The diffractograms at elevated temperature were measured in the sample holder, which did not diffract in the region of $2\theta < 5\text{-}40^\circ$. Its inner part was heated to the derived temperature with ultrathermostated water. The diffraction patterns obtained were indexed and theoretical powder diffractograms were calculated according to the program [8].

The electronic spectra were recorded on a Specord M 40 spectrophotometer (Carl Zeiss, Jena) in the region 11, 000-31, 000 cm^{-1} and on a Unicam SP 700 instrument in the region 4, 000-16, 000 cm^{-1}. The IR spectra were measured with a Pye Unicam SP 700 instrument in the region 200-4000 cm^{-1}. Both electronic and IR spectra were taken in Nujol suspensions.

The thermal decomposition of the studied compounds was followed on an OD 102 derivatograph (MOM, Budapest). The sample weight was 200 mg, the heating rate was ~3 deg min^{-1}, and the reference material was α-Al_2O_3. Measurements with sample weights of ~1 mg were performed on Perkin-Elmer TGS-1 thermobalance, at a heating rate of 5 deg min^{-1}. Both types of experiments were run in a dynamic air atmosphere. Before measurements, the samples were powdered and sieved to a mesh size of 0.18. The microphotographs of the crystals of $K_2[Cu(H_2O)_6](SeO_4)_2$ and those of two intermediates of its decomposition were taken on a JEOL JSM 35 microscope.

Thermogravimetric curves were analysed for kinetic data by using the Coats-Redfern method [9] as well as the equations which express the geometrical mechanism of reactions , collected in the computing program [10]. The least squares procedure was used for the calculations according to [9]; the reaction order was chosen from five values (0, 1/3, 1/2, 2/3 and 1) according to the criterion of the best linearity. The reaction mechanism according to [10] was chosen by using the criterion of the largest interval of linearity and the smallest standard deviation calculated for g(α).

Results and discussion

a. Structural changes of studied complexes during heating, and the stoichiometry of their decomposition.

The thermal decompositions of the Cu(II) and Ni(II) compounds of the type $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$ exhibit different stoichiometries. The dehydration of the Cu(II) compounds proceeds in two steps (except for the Cs salt):

$$M^I_2[Cu(H_2O)_6](SeO_4)_2 \rightarrow M^I_2(SeO_4)_2.2H_2O \rightarrow M^I_2Cu(SeO_4)_2$$

The decomposition of $Cs_2[Cu(H_2O)_6](SeO_4)_2$ proceeds in the same steps as found for its sulphato analogue [2] and can be described by the following scheme:

$$Cs_2[Cu(H_2O)_6](SeO_4)_2 \rightarrow Cs_2[Cu(H_2O)_4](SeO_4)_2 \rightarrow Cs_2Cu(SeO_4)_2.H_2O \rightarrow Cs_2Cu(SeO_4)_2.0.25H_2O \rightarrow Cs_2Cu(SeO_4)_2$$

The nickel(II) compounds decompose in one step:

$$M^I_2[Ni(H_2O)_6](SeO_4)_2 \rightarrow M^I_2Ni(SeO_4)_2 \quad (M^I = NH_4, Rb, Cs \text{ and } Tl)$$

For the potassium salt, the decomposition stoichiometry depends on the age of the compound. Freshly prepared samples decompose according to the scheme

$$K_2[Ni(H_2O)_6](SeO_4)_2 \rightarrow K_2[Ni(H_2O)_5](SeO_4)_2 \rightarrow$$
$$\rightarrow K_2Ni(SeO_4)_2.H_2O \rightarrow K_2Ni(SeO_4)_2$$

After longer standing $K_2[Ni(H_2O)_2](SeO_4)_2$ is formed as the product of the first decomposition reaction. The temperature intervals in which the described reactions take place are given in Table 2. Variation of the sample mass (appr. 200 times) did not cause any changes in the stoichiometry of the first decomposition steps; the decomposition temperatures were higher (Table 2) under these conditions and the stoichiometry of the further decomposition steps was also changed.

Table 2 The stoichiometry and temperature intervals of the dehydration of the compounds $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$

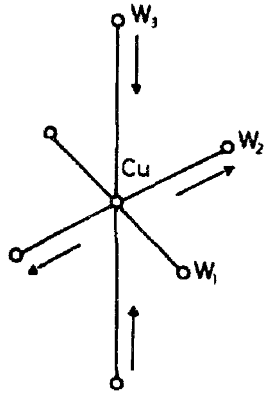
M^{II}	M^I	m mg	Stoichiometry of decomposition	Temperature intervals, °C
Cu	NH_4	200	-4, $-2H_2O$	55-104, 104-130
		1.082	-4, -1, $-1H_2O$	97-132, 132-150, 150-
	K	200	-4, $-2H_2O$	56-90, 128-150
		1.038	$-4H_2O$	87-104
	Rb	200	-4, $-2H_2O$	56-99, 106-168
	Tl	200	-4, $-2H_2O$	56-97, 97-130
		1.110	-4, $-1H_2O$	88-115, 115-125
Ni	NH_4	200	$-6H_2O$	84-181
		1.076	$-6H_2O$	111-169
	K	200	-4, $-2H_2O$	90-125, 217-270
		1.040	$-5H_2O$	113-157
	Cs	200	$-6H_2O$	93-189
		1.112	$-6H_2O$	120-173
	Tl	200	$-6H_2O$	88-184
		1.072	$-6H_2O$	119-153

If the observed decomposition stoichiometries are correlated with the structures of the Cu(II) and Ni(II) coordination polyhedra, it can be said that they agree approximately with the room-temperature structures only for the Ni(II) compounds. Their coordination polyhedra are nearly octahedral, as it was found for $(NH_4)_2[Ni(H_2O)_6](SeO_4)_2$ [11] at room-temperature.

Table 3 Interatomic distances Cu - Ow in the complexes $M^I_2[Cu(H_2O)_6](EO_4)_2$

M^I	E	r(Cu -Ow1), pm	r(Cu - Ow2), pm	r(Cu - Ow3), pm	Ref.
NH_4	S	196.6	207.3	223.0	15
K		194.4	206.8	227.9	23
Rb		195.7	203.1	230.7	25
Cs		196.6	200.4	231.4	24
Tl		195.7	201.7	231.7	26
NH_4	Se	199.0	203.1	223.7	13
K		193.7	204.4	229.7	21

Heating of this compound at the decomposition temperature did not cause anymarked changes in its powder pattern, except for very small shifts of the diffraction angels, which are probably connected with the thermal expansion of the elementary cell, or with analogous changes in the coordination polyhedra, as described below for the Cu(II) compounds. In the last case, six equivalent $Ni-OH_2$ bonds would be formed around the Ni(II) atom, which is in accordance with the observed decomposition stoichiometry. However, on the basis of our data, a different symmetry of the cation $[Ni(H_2O)_6]^{2+}$ should be assumed in the potassium salt.



Scheme 1 The coordination polyhedron of the Cu(II) in the studied compounds

In contrast with the Ni(II) compounds, the coordination polyhedra of Cu(II) in the cations $[Cu(H_2O)_6]^{2+}$ are frequently rhombically distorted, with three non-equivalent pairs of Cu-OH_2 bond distances (Table 3, Scheme 1) [12]. As the crystallographic data indicate, one of these pairs is considerably longer than the remaining two. One might therefore expect the release of only two water molecules in the first step of decomposition of the compounds with a rhombic $[Cu(H_2O)_6]^{2+}$ cation. This type of decomposition stoichiometry was found only for compounds containing a tetragonal cation $[Cu(H_2O)_6]^{2+}$ [1]. We therefore presumed structural changes of the Cu(II) coordination polyhedron during the heating.

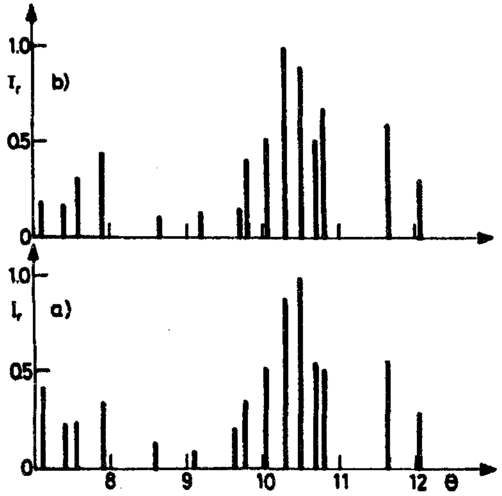


Fig. 1 Powder diffractograms of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ at
a) room temperature
b) 50 °C

Powder diffractograms of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ taken at 50° were slightly, but significantly different from those taken at room-temperature (Fig. 1). The changes in the relative intensities of the absorption lines were found to be reproducible and reversible. The diffraction lines were indexed according to the structure data [13]. The comparison with the model of its structure, and also the computed structure factors F_{hkl}, showed that the most pronounced differences were registered for the planes in which the oxygen atoms from the molecules W_3 and W_2 (Scheme 1) lie. Theoretical diffraction patterns were then calculated for different changes of Cu-OH_2 bond lengths and angles. Some examples are given in Table 4. The best coincidence between experimental and calculated patterns was achieved when shortening of the axial Cu-OH_2(W_3) bonds and lengthening of the originally longer equatorial Cu-OH_2(W_2) bonds was assumed (Table 4).

Table 4 Experimental and calculated relative intensities of diffraction lines in powder diffractograms of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ at room temperature and at 50°C

Plane	Experimental				Calculated					
(hkl)	room temp.		50°C		1		2		3	
	θ,°	I_r	θ,°	I_r	θ,°	I_r	θ,°	I_r	θ,°	I_r
100	7.1	0.425	7.02	0.205	7.07	0.38	7.07	0.32	7.07	0.36
111	7.9	0.345	7.9	0.47	7.99	0.42	7.99	0.42	7.99	0.42
012	10.30	0.847	10.32	1.00	10.36	1.00	10.36	0.89	10.36	1.00
102	10.50	1.00	10.52	0.877	10.51	0.91	10.51	1.00	10.51	0.95
031	11.65	0.460	11.72	0.603	11.73	0.85	11.73	0.80	11.73	0.83

Calculation No	Changes in the bond distances, , pm Cu - O_{W1}	Cu - O_{W2}	Cu - O_{W3}
1	0	+2.9	+2.3
2	0	+2.9	-3.7
3	0	+6.9	-3.7

In this way, four nearly equivalent Cu-OH_2 bonds are formed, most probably being distinctly longer than the remaining two Cu-OH_2 bonds in the Cu(II) coordination polyhedron. The changes in the symmetry of the Cu(II) coordination polyhedra derived from the high-temperature diffraction pattern are consistent with the trend of the Cu-OH_2 bond lengths in $M^{I}_{2}[Cu(H_2O)_6](SO_4)_2$ (M^{I} = NH_4, Rb) when heated from liquid nitrogen temperature to room-temperature [4, 14]. The same trend, i.e. the formation of equivalent Cu-N bonds, due to the dynamic Jahn-Teller effect at high temperatures, was observed for the complexes $M^{I}_{2}Pb[Cu(NO_2)_6]$ [5]. Moreover, in the isostructural compound $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, the water molecules W_3 and W_2 have $\Delta U_{ii}^{1/2}$ values (ΔU_{ii} = anisotropic temperature factor in the respective direction, $\Delta U_{ii}^{1/2}$ = $[U_{ii}(Cu) - U_{ii}(O)]^{1/2}$ in the bond direction) much higher than those of the remaining two water molecules [15]. The values of $\Delta U_{ii}^{1/2}$ reflect (at least to some extent) the freedom of the Cu-OH_2 bond movement [16] and were found to be important for the explanation of the thermal decomposition of Cu(II) compounds [6, 7]. The differences in the room-temperature and high-temperature powder patterns of $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ are not caused by the decomposition of the compound, as proved by chemical analysis and by the changes in the powder diffractograms.

Table 5 The absorption bands of selenato groups in the IR spectra of the compounds $M^I_2[Cu(H_2O)_n](SeO_4)_2$.

M^I	n	$\nu_1(SeO_4)$ cm^{-1}	$\nu_2(SeO_4)$ cm^{-1}	$\nu_3(SeO_4)$ cm^{-1}	$\nu_4(SeO_4)$ cm^{-1}
NH_4	6	830 w,br	340 w,sh 360 w,sh	870 s, br	420 s,br 440
	2	815 m	310 m	860 890 s 920 m	410 m 435 m 490 m
K	6	830 w, sh	350 m	890 s, br	425 s, br 435 s, br
	2	835 s	310 vw	885s 890 sh	400 vs, br 495 s
Rb	6	830 s		850 s 890 sh	420 w
	2	810 s	320 vw	860 s 880 s 905 m 920 m	405 s,br 430 s, br 505 m
Tl	6	820 s	335 w 360 m	850 s,br 870	405 420 s,br 430s, br 440
	2	810 s	340 sh	845 s 870 s	395 s,br 420 s,br 490 s

Abbreviations: s-strong, m-medium, w-weak, v-very, br-broad, sh-shoulder, After repeated heating of the compound to the decomposition temperature, the relative intensity of the (111) plane absorption line was not changed, in spite of the fact that this line is present in the pattern of the dihydrate, too. Moreover, all changes in the diffraction patterns of the hexahydrate compounds were found to be reversible.

Table 6 The electronic spectra of compounds $M^I_2[Cu(H_2O)_n](SeO_4)_2$

M^I	$\nu_{max}(d\text{--}d)$, cm^{-1}				
	n = 6		n = 2		
NH_4	12000	6200		12600	
K	12250	8200		12300	(5650)
		7200			
Rb	11900	--^{x}	23700	12600	--^{x}
Cs	12200	8150			
Tl	12000	8050	24000	12600	(6500)

x do not measured

The release of the water molecules from the coordination polyhedron of the Cu(II) leads to the coordination of the selenato groups, as can be seen from the IR spectra of the hexa- and dihydrates of the Cu(II) compounds (Table 5), as well as from the IR spectra of $K_2[Ni(H_2O)_n](SeO_4)_2$ ($n = 6, 2$). The symmetry of the SeO_4^{2-} anion is lower than T_d in all the studied hexahydrates, for the ν_1 and ν_2 vibrations of this group occur in all the IR spectra although they are forbidden for T_d symmetry. This symmetry lowering is due to hydrogen-bond formation. The splitting of the ν_3 and ν_4 vibrations was also observed in the IR spectra of the copper(II) dihydrates, indicating C_{3v} effective symmetry of the SeO_4^{2-} group in most cases. For the ammonium and rubidium salts, C_{2v} symmetry of the selenato group can be assumed. The electronic spectra of the copper compound dihydrates (Table 6) are typical for hexacoordinated Cu(II), and thus it must be concluded that four coordination sites are occupied by oxygen atoms from the selenato groups. The same conclusion holds for $K_2Ni(SeO_4)_2.2H_2O$. The dehydration of the studied Cu(II) compounds is associated with a blue shift of the main *d-d* transition bands, this shift being less marked than that found for the sulphato analogues [2]. The low-energy *d-d* transition bands were shifted to lower energies, or disappear. In the high-energy part of the electronic spectra of $Rb_2Cu(SeO_4)_2.2H_2O$ and $Tl_2Cu(SeO_4)_2.2H_2O$, weak bands centred at 24 000 cm^{-1} appear. According to their low intensity, these bands indicate the possible presence of binuclear species [18] with chelate coordination of the selenato groups. The latter assumption is supported by the presence of strong absorption bands in the IR spectra, at 505 cm^{-1} for the Rb^I salt and at 490 cm^{-1} for the Tl^I salts, attributed [19] to chelate-bonded EO_4^{2-} groups. Absorption at this wavelength was registered for other studied compounds as well, but no high-energy absorption was noted in the electronic spectra of compounds with M^I = NH_4 and K.

Concluding this part, we can state that the heating of the studied compounds, especially those with M^{II} = Cu, influences their structure, and mainly the Cu-OH_2 bond distances. The changes are clearly demonstrated in the stoichiometry of thermal decomposition of the compounds $M^I_2[Cu(H_2O)_6](SeO_4)_2$. In the course of the decomposition, the originally outer sphere anions are coordinated to the central atoms, so that the coordination number remains six in the intermediates and products of the decomposition [20].

b. Kinetic study of the first dehydration step for the compounds $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$.

Table 7 Influence of the experimental conditions on the activation parameters of the first dehydration reaction of the compound $K_2[Cu(H_2O)_6](SeO_4)_2$

Sample mass, mg	Heating rate, K min^{-1}	E* kJ mol^{-1}	log A	E* kJ mol^{-1}	log A
		Coats-Redferm		Škávra-Šesták	
100	1.5	215.6 ±6.6	31.2 ±1.0	164.7 ±5.1	22.6 ±0.7
100	3	166.1 ±6.8	23.1 ±1.0	119.4 ±5.8	15.4 ±0.8
200	1.5	160.6 ±3.7	22.2 ±0.6	155.7 ±5.1^a	20.0 ±0.8^a
200	3	123.6 ±1.5	13.4 ±0.4	88.2 ±1.3	12.1 ±2.2
1.038	5	364	24		

Reaction order according to Coats-Redfern: n = 1
Reaction mechanism according to Škvára-Šesták: a D3 $g(\alpha) = [(1+\alpha)^{1/2} - 1]^2$
others: R3 $g(\alpha) = [1 - (1-\alpha)^{1/3}]^{1/3}$

The influence of the experimental conditions (sample weight, heating rate) on the reaction order, activation energy and pre-exponential factor was investigated prior to the study of the relationship between the reaction kinetics and the structure of the decomposed compounds. Four series of experiments (each with five parallel investigations) were run on the compound $K_2[Cu(H_2O)_6](SeO_4)_2$. The values of activation energy (E^*) and pre-exponential factor (A) decrease with increasing heating rate and sample mass

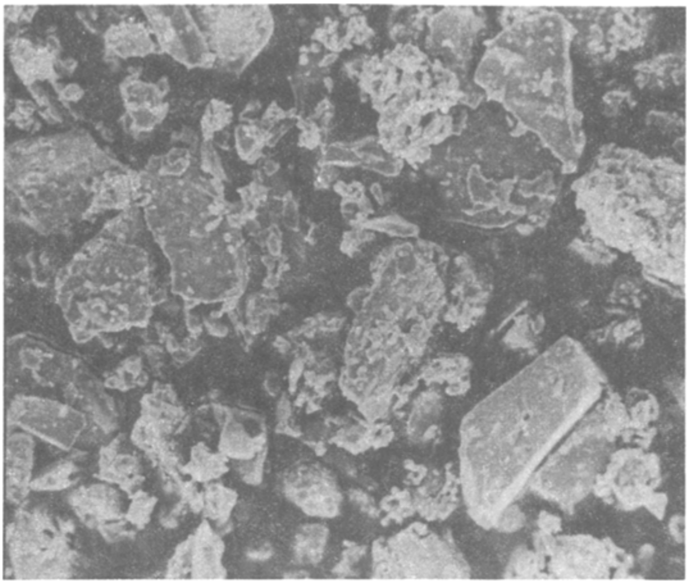


Plate 1 Microphotographs of $K_2[Cu(H_2O)_6](SeO_4)_2$, $\alpha = 0$,
a) 100x

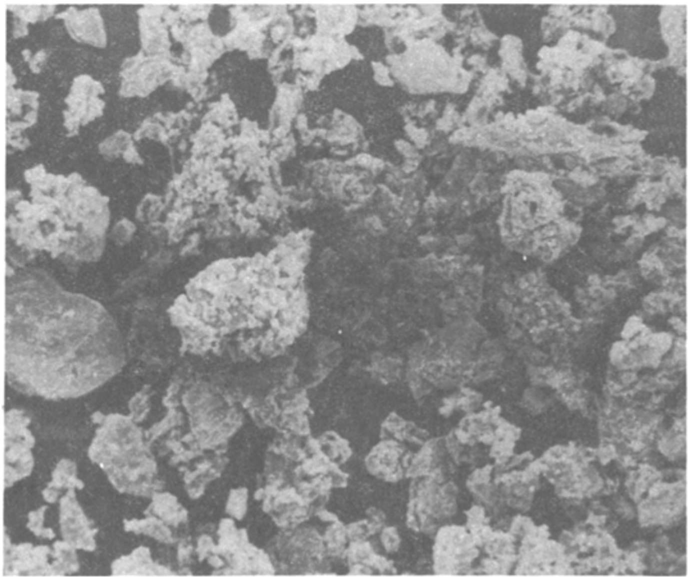


Plate 2 Microphotographs of the intermediate of the thermal decomposition of the $K_2[Cu(H_2O)_6](SeO_4)_2$, $\alpha = 0.134$,
a) 100x

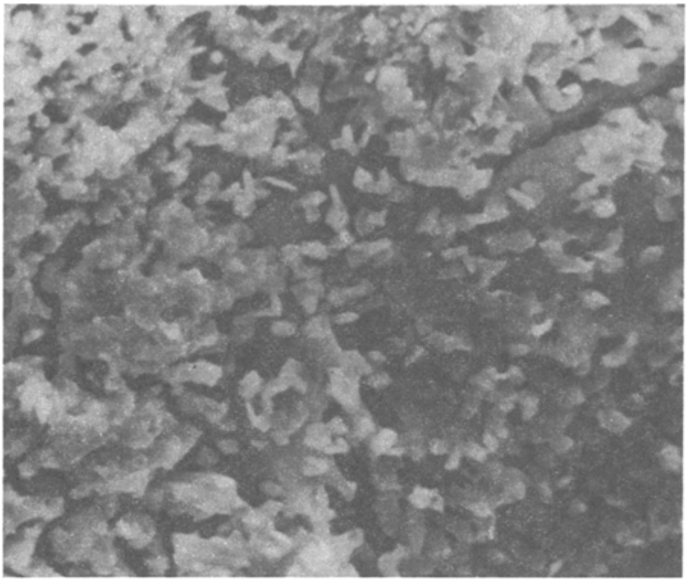


Plate 2 Microphotographs of the intermediate of the thermal decomposition of the $K_2[Cu(H_2O)_6](SeO_4)_2$, $\alpha = 0.134$, b) 2000x

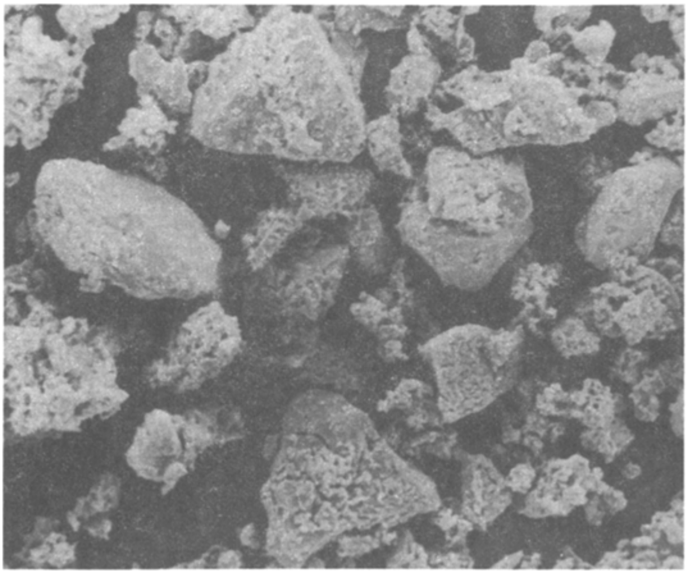


Plate 3 Microphotographs of the intermediate of the thermal decomposition of the $K_2[Cu(H_2O)_6](SeO_4)_2$, $\alpha = 0.332$, a) 100x

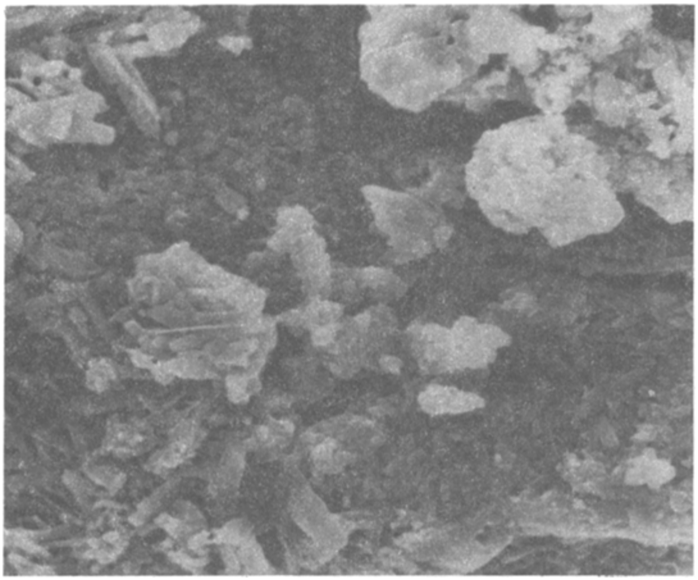


Plate 3 Microphotographs of the intermediate of the thermal decomposition of the $K_2[Cu(H_2O)_6](SeO_4)_2$, $\alpha = 0.332$, a) 2000x

(Table 7) and different values of E^* and A were gained according to [9] and [10], respectively. The measurements on the other complexes were then performed with sample mass 200 mg and heating rate 3 deg min^{-1}. The results of the kinetic evaluation of the TG curves are given in Table 8. For all compounds under study, the reaction order $n = 1$ was established according to [9]. The most probable reaction mechanism, according to [10], was the reaction on the phase boundary with spherical symmetry, denoted as R3 ($g(\alpha) = [(1-(1-\alpha)^{1/3}]^{1/3}$), or three-dimensional diffusion, denoted as D3 ($g(\alpha) = [(1+\alpha)^{1/2} -1]^2$) . In some cases it was not possible to decide which type of mechanism is the ruling one. In these cases the two most probable mechanisms are given. The program [10] also allows separate investigation of the initial stages of reaction. This was done for all compounds, but different results were obtained only for the ammonium-copper and potassium copper compounds (Table 8), the activation energies and pre-exponential factors being greater in the early stages of the reactions. The kinetic data obtained suggested that the dehydration is in most cases controlled by the chemical reaction on the phase boundary and the activation parameters are relevant for the chemical reactions. However, the dependence of E^* and A on the experimental conditions suggests a considerable difference between on the experimental conditions suggests a considerable difference between the experimental and real values of both parameters. To acquire more information on the reaction course, microphotographs of polycrystalline $K_2[Cu(H_2O)_6](SeO_4)_2$ in different stages of decomposition were taken. These showed that the nuclei of the new phase are present on the sample surface at the beginning of the decomposition (Plate 1). The formation of the new phase does not proceed in the whole sample volume, because the lustre surfaces of the original phase can be seen in the pictures even at α = 0.13 (Plate 2). We conclude that, at least in these stages of the reaction, the nucleation and the diffusion are not the slowest processes. When α reaches a value of 0.34 (Plate 3), only the microcrystals of the new phase are visible in the pictures. However, they do not form a compact layer, and the chemical reaction is again the rate-contrroling process.

A comparison of the E^* values found for the first decomposition reactions of the complexes $M^I_2[Cu(H_2O)_6](SeO_4)_2$ with those for the sulphato analogues [2] showed that the trend in the variation of the E^* values with the counter-ion M^I are analogous, but not identical. The activation energies corresponding to the first dehydration reaction of the sulphato compounds increase with increasing degree of tetragonal deformation of the coordination polyhedra $[Cu(H_2O)_6]^{2+}$ [2]. This is not true for the selenato compounds with known crystal structures. The tetragonal deformation of the coordination polyhedron was found to be greater in $K_2[Cu(H_2O)_6](SeO_4)_2$ [21] than in the ammonium salt [13]; the obtained E^* value is greater for the ammonium salt (Table 8). As concerns the structural changes of the cation $[Cu(H_2O)_6]^{2+}$ during heating, we concluded that the Cu-O_{W2} bond length in the equatorial plane of the copper(II) may be the structural factor influencing the dehydration kinetics. A comparison of the activation energies with these bond lengths for all compounds $M^I_2[Cu(H_2O)_6](EO_4)_2$ with known crystal structures showed that the activation energy values increase with decreasing Cu-O_{W2} bond distance.

The values of E^* and log A obtained with both methods for the studied Cu(II) compounds lie in the sequence

$$Tl > Rb > NH_4 > K$$

For the Ni(II) compounds, a quite different sequence of these values was found:

$$K > Tl > NH_4 > Rb > Cs$$

We therefore presume that the differences in the E^* and log A values found for the first dehydration reactions of the Cu(II) compounds are not due solely to the different electrostatic interactions in the crystals of the studied complexes as a consequence of the presence of different counter-cations M^I.

Table 8 Kinetic parameters for the first dehydration reaction of the compounds $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$

M^{II}	M^I	Coats-Redfern			Škvára-Šesták		Mecha-nism
		E* kJ mol^{-1}	log A	n	E* kJ mol^{-1}	log A	
Cu	NH_4	143.9±4.3	15.20±0.66	1	148.5±5.9[a]	19.45±1.34[a]	R3
					128.3±4.6[b]	15.70±0.60[b]	R3
	K	123.6±1.5	13.36±0.40	1	131.2±7.0[a]	18.50±0.99[a]	R3
					88.2 ±1.3[b]	12.09±2.15[b]	R3
	Rb	177.3±6.3	20.84 0.87	1	125.9±2.2	17.47± 0.33	R3
					165.8±5.6	22.10±0.48	D3
	Tl	180.7± 9.6	21.66±1.43	1	157.1±7.5	22.25±1.00	R3
Ni	NH_4	91.0± 3.1	8.91±0.46	1	128.5±1.3	13.70±0.54	R3
	K	190.3±8.8	23.83±1.26	1	144.5±9.2	16.97±1.22	R3
					195.1±5.9	23.14±0.68	D3
	Rb	83.6±4.8	7.77±0.65	1	123.7±6.7	13.97±1.51	R3
	Cs	75.3±5.6	6.96±0.75	1	105.6±4.5	10.77±0.59	R3
					131.7±4.3	13.31±0.57	D3
	Tl	100.2±4.2	10.11±0.61	1	114.9±5.8	11.69±0.82	R3

[a] α <0.06-0.6>; [b] α <0.2-0.8>

For the compounds of Ni(II), only the crystal structures of $(NH_4)_2[Ni(H_2O)_6](EO_4)_2$, with E = S [22] and Se [11], have been solved. Shorter Ni-H_2O bonds were found in the sulphato compound. In accordance with this, the activation energy for the dehydration was found to be higher for the sulphato [2] than for the selenato compound of Ni(II).

In conclusion, we can say that both the activation energies found from the thermogravimetric experiments on the dehydration of compounds $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$, and also the pre-exponential factors, are the higher, the shorter one pair of the split bonds. We presume that the activation of these compounds comprises the formation of octahedral $[Ni(H_2O)_6]^{2+}$ cations with six nearly equivalent bonds, or compressed tetragonal $[Cu(H_2O)_6]^{2+}$ cations with four nearly equivalent M-H_2O bonds.

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Zusammenfassung - Zur Aufklärung des Zusammenhanges zwischen dem Zersetzungsweg und der bekannten Kristallstruktur wurde die thermische Dehydration der Verbindungen $M^I_2[M^{II}(H_2O)_6](SeO_4)_2$ mit M^I = NH_4, K, Rb, Cs and Tl sowie mit M^{II} = Cu und Ni untersucht. Man fand für diese Reaktion die gleiche Stöchiometrie wie für die analogen Sulfatverbindungen von Cu(II) bzw. Ni(II). Wegen des Widerspruches zwischen der Kristallstruktur bei Raumtemperatur und der festgestellten Stöchiometrie der Zersetzungsreaktion wurden auch Pulverdiffraktionsaufnahmen bei höheren Temperaturen angefertigt. Bei Cu(II)-Verbindungen konnte während des Erhitzens eine Strukturänderung festgestellt werden. Für verschiedene Strukturänderungen wurden Pulveraufnahmen berechnet und mit den experimentellen verglichen. Es konnte gezeigt werden, da sich während des Erhitzens zwei axiale Cu-H_2O-Bindungen verkürzen und zwei äquatoriale Bindungen strecken. Die beobachtete Zersetzungsstöchiometrie entspricht der Bildung von vier anänhernd gleichen Cu-H_2O-Bindungen. Die Aktivierrungsenergie (E^*) und der präexponentielle Fak-

tor (log A) und der ersten Dehydratationsreaktion der Cu(II)-Verbindungen sinken in folgender Reihenfolge für M^I: Tl, Rb, NH_4, K und sind umso größer, je kürzer die gespaltenen äquatorialen Cu(II)-Bindungen sind. Für Ni(II)-Verbindungen nehmen E^* und log A in folgenden Reichenfolge ab: K, Tl, NH_4, Rb, Cs.