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

Stoichiometry and kinetics of thermal decompositions of complexes $Cu(H_2O)_6X_2(X^- = C_6H_5SO_3, 4\text{-}CH_3C_6H_4SO_3$ and $D\text{-}C_{10}H_{15}OSO_3)$

H. Langfelderová, M. Linkešová, P. Ambrovič
and *A. Riedlmajerová*

DEPARTMENT OF INORGANIC CHEMISTRY, SLOVAK TECHNICAL UNIVERSITY,
812 37 BRATISLAVA, CZECHOSLOVAKIA
+INSTITUTE OF POLYMERS, SLOVAK ACADEMY OF SCIENCES,
842 36 BRATISLAVA, CZECHOSLOVAKIA

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The stoichiometry and the kinetics of thermal decomposition of the title compounds were studied. The results were correlated with the structures of the Cu(II) coordination polyhedra, which have in general a 4+2 type of coordination. It was shown that the equatorial Cu–H_2O bond distances are important for the found decomposition stoichiometries. As an intermediate of thermal decomposition, $Cu(H_2O)_5(CH_3C_6H_4SO_3)_2$ was prepared and characterized via its IR and electronic spectra and powder X-ray diffractogram. The experimental activation energies increase with increasing degree of tetragonality of the Cu(II) coordination polyhedron for $X^- = C_6H_5SO_3$ and $D\text{-}C_{10}H_{15}OSO_3$, but decrease for $X^- = 4\text{-}CH_3C_6H_4SO_3$. The E^* value found for the decomposition of the latter compound can not be attributed to the chemical reaction.

We earlier pointed out that the reactivity of copper(II) coordination compounds depends, among others, on the structure of the coordination polyhedra of the decomposed complex [1]. For compounds containing the cation $[Cu(H_2O)_6]^{2+}$, it was found that the activation energy (E^*) of their dehydration increases with increasing degree of tetragonal deformation [2] of the Cu(II) coordination polyhedron [3].

The cation $[Cu(H_2O)_6]^{2+}$ also occurs in the compounds $Cu(H_2O)_6X_2$, where X is benzenesulphonate, 4-toluenesulphonate or D-camphor-10-sulphonate [4]. It was therefore of interest to find out whether the interdependence between the structures of the coordination polyhedra and the trends in the experimental activation energy variations hold for these complexes, too. In contrast with the previously studied

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compounds $M^{I}_{2}[Cu(H_2O)_6](SO_4)_2$ [3], the complexes in the present investigation are not mutually isomorphous [4].

The question was whether, in spite of this fact, the differences in the deformations of the coordination polyhedra are reflected in the course of the thermal decompositions of the complexes $[Cu(H_2O)_2]X_2$.

Experimental

Chemicals

$CuSO_4 \cdot 5H_2O$, $Ba(OH)_2 \cdot 8H_2O$, $C_6H_5SO_3H$, 4-$CH_3C_6H_4SO_3H$, $DC_{10}H_{15}OSO_3H$, all p.a., LaChema Brno, ČSSR.

Syntheses

The studied complexes were prepared according to procedures given in [4]. The intermediates of their thermal decompositions were prepared by isothermal decomposition of the respective compounds. The decomposition temperatures were chosen on the basis of non-isothermal experiments.

Analytical methods

The C and H contents in the prepared complexes were found by elemental analysis, using an automatic Carlo Erba (Milano) analyser. The Cu content was found by complexometric titration with murexide as indicator. The results are given in Table 1.

Table 1 Analytical compositions of complexes $Cu(H_2O)_nX_2$

X^-	n	Cu, %		C, %		H, %	
		calc.	found	calc.	found	calc.	found
$C_6H_5SO_3$	6	13.075	13.10	29.66	29.40	4.53	4.46
	4	14.12	14.08	32.03	31.90	4.00	3.92
$CH_3C_6H_4SO_3$	6	12.36	12.26	32.71	32.65	5.10	5.38
	5	12.81	12.80	33.90	33.80	4.84	4.65
$C_{10}H_{15}OSO_3$	6	10.02	10.00	37.88	37.53	6.63	6.80
	2	11.30	11.24	42.78	42.65	6.05	5.95

Apparatus and measuring procedures

The thermal decompositions of the studied complexes were carried out on an OD–102 derivatograph (MOM, Budapest, Hungary). Samples were placed in ceramic crucibles with an upper diameter of 14 mm. Temperature was measured with Pt–Pt, Rh thermocouples. The sample weight was 100 mg, and the heating rate 2.5 deg min^{-1}. Before measurements, all samples were finely powdered and sieved to a mesh size of 0.018. The experiments were also run on a Perkin–Elmer TG–1 instrument, with a sample weight of ~3 mg, and a heating rate of 5 deg min^{-1}.

Powder diffraction patterns were obtained on a GON–2 powder goniometer (Czechoslovakia); CuK_α radiation and Ni filter were used. The sample was placed in a holder, and heated to a temperature only slightly lower than the decomposition temperature of the parent compound. As the heating medium, circulating water was used, the temperature of which was controlled by an ultrathermostat.

Electronic and IR spectra of the studied compounds were run on a Unicam SP–700 spectrophotometer (7000–30,000 cm^{-1}) and on a Specord 75 IR (GDR) spectrophotometer (400–4000 cm^{-1}), respectively. In both experiments the Nujol technique was used.

The TG curves of the studied compounds were analysed for kinetic data by using the Coats–Redfern method [5] and also the equations which express the geometrical reaction mechanism, collected in the computing program [6]. For the evaluation of E^* values according to [5], the least-squares procedure was used, the reaction order being chosen from five values (0, 1/3, 1/2, 2/3 and 1) according to the criterion of the best linearity.

Results and discussion

A) Structural changes of complexes during thermal decomposition, and stoichiometry of thermal decompositions

Although the composition and the symmetry of the Cu(II) coordination polyhedra in the complexes under study are almost the same as in the compounds $M^I_2[Cu(H_2O)_6](SO_4)_2$ [7], the stoichiometry of the thermal decompositions of the complexes $Cu(H_2O)_6X_2$ is different for X = benzenesulphonate and 4-toluenesulphonate; in the presence of the D-camphor-10-sulphonate anion, the stoichiometry of the first decomposition step is the same as found for the complexes $M^I_2[Cu(H_2O)_6](SO_4)_2$ [3] (Table 2). The decomposition stoichiometries, at least in the first steps, are not changed due to variations in the experimental conditions.

In the powder X-ray patterns of the respective compounds, no changes were registered on heating to the decomposition temperature. It can therefore be

Table 2 Stoichiometries of thermal decomposition of complexes $Cu(H_2O)_6X_2$

X^-	Sample weight, mg	Number of water molecules released	Decomposition temperatures, °C
$C_6H_5SO_3$	100	−2, −2, −2	45, 84, 105
	3	−2, −2, −2	40, 72, 87
$CH_3C_6H_4SO_3$	100	−1, −1, −2, −2	36, 60, 78, 100
	3	−1, −3, −2	40, 54, 84
$C_{10}H_{15}OSO_3$	100	−4, −1, −1	40, 92, 148
	3	−4, −2	42, 82, 105

presumed that no significant changes took place in the overall or local symmetry of the studied compounds during their heating. Hence, we tried to correlate the found decomposition stoichiometries with the interatomic distances Cu–H_2O and with the symmetries of the parent coordination polyhedra. Rhombic deformation of the essentially tetragonal-bipyramidal coordination polyhedra, present in all hydrates of double copper(II) sulphates [7], was established only for the camphorsulphonate salt, and only this compound exhibits the same stoichiometry in the first decomposition step as do the compounds $M^I_2[Cu(H_2O)_6](SO_4)_2$. The rhombic deformation of the equatorial plane of the Cu(II) coordination polyhedron in the complex $[Cu(H_2O)_6](C_{10}H_{15}OSO_3)_2$ leads to unequal Cu–H_2O distances in this plane, two of these distances being markedly longer (205 and 207 pm, respectively) than the other one (197 pm) [4].

The coordination polyhedra in the benzene- and toluenesulphonate salts are almost not deformed rhombically (Table 5). However, the axial Cu–H_2O bond distances are considerably longer than the equatorial ones, and hence the decomposition stoichiometry found for the compound $[Cu(H_2O)_6](C_6H_5SO_3)_2$ can be explained on this basis, but not that found for $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$. For the last compound, however, the rows of $[Cu(H_2O)_6]^{2+}$ cations are surrounded by only two nearest rows of toluenesulphonate, whereas in the benzenesulphonate compound there are four such rows, the SO_3 groups being oriented in both cases to the nearest Cu(II) polyhedra.

The powder diffractograms of $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$ and $[Cu(H_2O)_5](CH_3C_6H_4SO_3)_2$ are not very different (Table 3). This suggests that in the first step of the decomposition very little, if any, structural changes take place. This was confirmed by calculation of theoretical diffraction patterns (according to [8]) for the initial complex and for the intermediate of thermal decomposition. The calculation for the latter compound was carried out on the basis of the crystal structure data on $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$; the occupation factor for the oxygen atom from the axially bonded water molecule was taken as 0.5. The coincidence between the calculated and experimental powder patterns is very good

Table 3 Experimental and calculated powder diffractograms of complexes $Cu(H_2O)_nX_2$

$Cu(H_2O)_6(CH_3C_6H_4SO_3)_2$					$Cu(H_2O)_5(CH_3C_6H_4SO_3)_2$				
	calculated		experimental			calculated		experimental	
hkl	θ	I/I_0	θ	I/I_0	*hkl*	θ	I/I_0	θ	I/I_0
020	3.44	100	3.45	100	020	3.44	96.7	3.03	17
040	6.89	14.8	6.90	15		3.95		3.95	100
100	7.86	24.0	7.85	24	040	6.89	16	6.9	11.6
031	8.11	88.9	8.10	55	100	7.86	31	7.8	12
121	9.32	32	9.40	28	031	8.11	100	8.1	20
131	10.1	44	10.07	32	121	9.32	44.5	9.3	17
140	10.5	37.1	10.4	35	131	10.10	53.8	10.3	33
111	11.43	30.6	11.4	28	140	10.48	46	10.6	32
131	12.47	11.4	12.5	10					
002	12.56	14.4							

$Cu(H_2O)_6(C_6H_5SO_3)_2$					$Cu(H_2O)_4(C_6H_5SO_3)_2$	
	calculated		experimental		experimental	
hkl	θ	I/I_0	θ	I/I_0	θ	I/I_0
200	3.93	100	3.8	100	3.4	74
400	7.80	14.2	7.85	16.5	3.85	28
					7.65	25
210	8.11	13	8.05	17.3		
301	8.93	48	8.85	45	8.7	73
					8.9	78
011	9.33	66	9.25	34	9.1	97
					9.65	55
311	10.86	2.5	10.8	40	10.8	100
	11.28	2.8	11.4	45		
	11.58	1.5	11.8	57	11.85	60
411	12.02	7.2	12	45	12	71.5
022	12.82	25	12.8	25	12.4	60

(Table 3). It can be concluded that in the first step of $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$ thermal decomposition the axially bonded water molecules are evolved statistically. Probably this decomposition mechanism is responsible for the found decomposition stoichiometry and for the low experimental activation energy for this reaction.

The picture is quite different for the intermediate of $[Cu(H_2O)_6](C_6H_5SO_3)_2$ decomposition. The powder diffractogram of the tetraaqua complex differs significantly from that of the initial compound and can not be calculated on the basis of the crystal structure data on the latter compound (Table 3). Therefore, quite significant structural changes must be considered for the first step of thermal decomposition of $[Cu(H_2O)_6](C_6H_5SO_3)_2$.

The electronic spectra of the intermediates of decomposition of all three compounds under study again indicate different changes in the deformation of the parent Cu(II) coordination polyhedra. Very small differences were found between the Cu(II) coordination polyhedra in the benzene- and toluenesulphonate compounds and their decomposition intermediates, respectively (Table 4). However, for the hexa- and dihydrates of the camphorsulphonate, a blue shift of 500 cm^{-1} of $\tilde{\nu}_{max}(d-d)$ was observed during the dehydration.

The IR spectra of the starting compounds and of the thermal decomposition intermediates (Table 4) indicate that the —SO_3 groups substitute the water molecules during this process. The most significant changes were found for $\nu_s(SO_3)$ and $\nu_{as}(SO_3)$, and for $\delta_{as}(SO_3)$ and $\delta_s(SO_3)$. If the IR spectrum of $C_6H_5SO_3^-$ in its sodium salt [9] is compared with that of $[Cu(H_2O)_6](C_6H_5SO_3)_2$, it is obvious that the symmetry of the —SO_3 group is lowered in the latter compound, due to hydrogen-bonds formation. It is interesting, however, that no absorption maxima

Table 4 IR and electronic spectra of complexes $Cu(H_2O)_nX_2$ (all in cm^{-1})

X	$C_6H_5SO_3$[a]		$CH_3C_6H_4SO_3$[b]		$C_{10}H_{15}OSO_3$[a]	
$n=$	6	4	6	5	6	2
$\nu_{as}(SO_3)+$	571 s	565	557 m	557 m	580 m	565 m
$\nu_s(SO_3)$	600 s	600 s				590 vm
$\varrho(H_2O)+\nu_s(SO_3)$	855	840	807	807	823 w	826 w, sh
			853	853	850 w	856 w
					857 w	
$\nu_s(SO_3)$	1014 s	1013 s	1010	1010		
	1035 s	1037 s	1037	1035	1035 s	1040 vs
					1050 vs	1055 vs
	1070 s	1070 vw	1115 sh	1110 sh		1070 s
$\nu_{as}(SO_3)$	1127 vs	1127 vs	1130 s	1130 s	1120 m	1133 vs
	1180 vs	1150 vs	1164 s	1164 s	1170 vs	1150 vs
		1225 vs	1200 vs	1200 vs	1210 m	1220 vs
			1226 vs	1225 m	1260 w	1243 vs
						1263
			1280 w, sh	1280 w, sh		1290 s
$\delta(H_2O)+$	1640				1635 s	1630 s
$\nu(C—H)$					1640 s	
	1650 sh	1650 sh	1650 vs	1650 vs		
$\tilde{\nu}_{max}$ $d-d$	11800	11900	12500	12500	11500	12000

The absorption bands were assigned according to *a* [9], *b* [10]. Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder.

were registered in the region 1220–1240 cm^{-1}, corresponding to the $\nu_{as}(SO_3)$ vibrations in the spectrum of the hexaaqua compound, but they did appear in the spectrum of the tetrahydrate. Dehydration of the hexaaquacopper(II) benzenesulphonate to the tetrahydrate was also accompanied by a shift of $\nu_{as}(SO_3)$ from 1180 to 1150 cm^{-1} and of $\varrho(H_2O)$ from 855 to 840 cm^{-1}. Dehydration of the hexaaquacopper(II) camphorsulphonate to its dihydrate led to very marked changes in the IR spectrum. Nearly all the absorption bands corresponding to the —SO_3 group vibrations changed their positions and/or their relative intensities. With regard to hexacoordination of the Cu(II) in $Cu(H_2O)_2(C_{10}H_{15}OSO_3)_2$ too, we have to assume the coordination of —SO_3 groups to at least two neighbouring Cu(II) atoms. In contrast, no differences between the IR spectra of $[Cu(H_2O)_n](CH_3C_6H_4SO_3)_2$ ($n = 5, 6$) were observed. This is in agreement with the data from other methods, which indicate no structural changes in this step of the decomposition.

It should be mentioned that the compositions of the first intermediates formed in the decompositions of compounds with $X^- = C_6H_5SO_3$ and $CH_3C_6H_4SO_3$ are rather unusual for Cu(II) compounds.

B) Kinetic analysis of thermal decompositions

The results of kinetic analysis of the first step of the thermal decompositions of the complexes $Cu(H_2O)_6X_2$ are given in Table 5. From the data on the reaction mechanism, it can be assumed that the reactions proceed on the phase boundary with spherical symmetry, the rate-controlling process being the chemical reaction accompanied by the above-discussed structural changes. The kinetic parameters for the decomposition of $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$ (sample weight 100 mg) were calculated for the formation of the tetrahydrate, because of uncertainty in the estimation of α for the formation of the pentaaqua complex under non-isothermal experimental conditions. The results of the two methods used for estimation of the activation energies (E^*) and pre-exponential factors (A) are different, but they follow the same trend. The data obtained on the smaller samples ($\sim$4 mg) showed (Table 5) that the numerical values of E^* and A calculated according to [6] are more reliable for the benzenesulphonate and camphorsulphonate compounds. Considerable difficulties arose in the kinetic evaluation of the TG curves of the toluenesulphonate compound with a sample weight of $\sim$4 mg. These experimental conditions led to a better resolution of the first decomposition step, and therefore the formation of the pentaaqua compound was evaluated. However, no reasonable E^* and A values were obtained with α in the range $\langle 0.08\text{–}0.85 \rangle$, both values being too high ($E^* > 350$ kJ mol^{-1}, $A > 10^{35}$ s^{-1}) for normal dehydration reactions. Lower values of both were achieved only when they were calculated for rather

Tafle 5 Kinetic parameters for first step of thermal decomposition of complexes $Cu(H_2O)_6X_2$ in correlation with interatomic distances Cu–OH_2

X^-	m, mg	Coats–Redfern [5]		Škvára–Šesták [6]				Interatomic distances, pm			
		E^*, kJ · mol^{-1}	A^*, s^{-1}	n	E^*, kJ · mol^{-1}	A^*, s^{-1}	mechanism	R_e^1	R_e^2	R_a	T
$C_6H_5SO_3$	100	142 ± 5	$1.5 \cdot 10^{19}$	1	116 ± 6	$6.6 \cdot 10^{14}$	R_3	197.9	198.6	226.4	0.871
								195.8	196.1	225.9	0.871
$CH_3C_6H_4SO_3$	100	111 ± 2	$6.5 \cdot 10^{14}$	1	85 ± 5	$1.8 \cdot 10^{10}$	R_3	195.3	195.4	242.3	0.806
$C_{10}H_{15}OSO_3$	100	129 ± 7	$1.7 \cdot 10^{17}$	1	110 ± 4	$9.4 \cdot 10^{13}$	R_3	205.0	197.0	217.0	0.912
								197	202	222	0.912
$C_6H_5SO_3$	4.162	120	$5.1 \cdot 10^{17}$	2/3	121	$2.7 \cdot 10^{15}$	R_3				
$C_{10}H_{15}OSO_3$	4.918	109	$3.9 \cdot 10^{13}$	1	102	$5.3 \cdot 10^{11}$	R_3				

Reaction mechanism R_3: the reaction proceeds on the phase boundary with spherical symmetry, $g(\alpha) = [1-(1-\alpha)^{1/3}]^{1/3}$.

* Geometrical mean of estimated values.

narrow intervals of α. The E^* value in the interval of α $\langle 0.55\text{–}0.85\rangle$ was 136 kJ mol^{-1}, for the interval $\langle 0.35\text{–}0.60\rangle$ it was 179 kJ mol^{-1}, and for the interval $\langle 0.35\text{–}0.80\rangle$ it was 159 kJ mol^{-1}, all for $n=0$. All these values are much higher than those given in Table 5. This fact can be explained by assuming changes in the reaction mechanism due to the change of the sample mass. The rate-controlling process in the decomposition of $[Cu(H_2O)_6](CH_3C_6H_4SO_3)_2$ is therefore most probably not the chemical reaction and the kinetic data are not relevant for the characterization of the relationship between the structures of the coordination polyhedra and the course of thermal decomposition.

On the other hand, the kinetic data on the decompositions of the benzene- and camphorsulphonates are in good agreement with our previous findings that the reactivities of the Cu(II) compounds depend on the structure of the Cu(II) coordination polyhedra. The influence of the overall crystal structures seems to be smaller, as follows from a comparison of the E^* values obtained in this work with those found for $M^I_2[Cu(H_2O)_6](SO_4)_2$ [2], with T values near to each other, but different crystal symmetries.

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Zusammenfassung — Die Stöchiometrie und Kinetik der thermischen Zersetzung der Titelverbidungen wurde untersucht. Die Ergebnissen wurden auf die Strukturen der Cu(II) Koordinationspolyeder bezogen, die im allgemeinen eine 4+2 Koordination aufweisen. Die Länge der äquatorialen Cu–H_2O Bindung erwies sich als bedeutungsvoll für die ermittelte Stöchiometrie der Zersetzung. Das Zwischenprodukt $Cu(H_2O)_5(CH_3C_6H_4SO_3)_2$ der thermischen Zersetzung wurde dargestellt und mittels

IR- und Elektronenspektren sowie Röntgenpulveraufnahmen beschrieben. Mit ansteigendem Tetragonalitätscharakter der Cu(II) Koordinationspolyeder wachsen die experimentell ermittelten Aktivierungsenergien für $X^- = C_6H_5SO_3$ und D–$C_{10}H_{15}OSO_3$ an, nehmen aber für $X^- =$ 4-$CH_3C_6H_4SO_3$ ab. Der für letztere Verbindung ermittelte E^* Wert kann der chemischen Reaktion nicht zugeschrieben werden.

Резюме — Изучена стехиометрия и кинетика термического разложения комплексов меди с некоторыми сульфокислотами. Результаты коррелировались со структурой координационного полиэдра меди, обладающего координацией типа 4+2. Показано, что длина экваториальной Cu–H_2O свази является важной характеристикой для найденной стехиометрии разложения. Полученный промежуточный продукт разложения $Cu(H_2O)_5(CH_3C_6H_4SO_3)_2$ охарактеризован оптическими спектрами, ИК спектроскопией и порошковой рентгено-диффрактограммой. Экспериментально найденные энергии активации увеличиваются с увеличением степени тетрагональности координационного полиэдра меди в комплексах с $X^- = C_6H_5SO_3$ и Д–$C_{10}H_{15}OSO_3$, но уменьшаются в комплексе с $X^- =$ 4-$CH_3C_6H_4SO_3$. Установленная энергия активации реакции разложения этого комплекса не может быть обусловлена химической реакцией.