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ON THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu^{II} COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS

III. STUDY OF THE EFFECT OF THE DISTORTION DEGREE OF THE Cu^{II} COORDINATION POLYHEDRON ON THE COURSE OF THERMAL DECOMPOSITION OF THE COMPLEXES $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$

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The thermal decomposition of the complexes $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ and $M_2Ni(SO_4)_2 \cdot 6\,H_2O$ (M^I = NH_4, K, Rb, Tl) containing the complex cation $M^{II}(H_2O)_6{}^{2+}$ (M^{II} = Cu, Ni) was studied. The values of the experimental activation energy E^* obtained for the dehydration reactions of both complex cations were found to be influenced in different ways by the outer-sphere cations present. It was therefore concluded that the activation energy of the decomposition of $Cu(H_2O)_6{}^{2+}$ depends on the degree of tetragonal distortion of this cation, which increases with the ionic radius of cation M^I. The ΔH values of the studied reactions depend less on the structures of the coordination polyhedra.

Due to the d^9 electron configuration of the central atom, the coordination polyhedron of Cu^{II} is known to be plastic [1]. The structure of the coordination polyhedron of this central atom (degree of distortion, coordination number etc.) can be affected by a number of factors, such as ligand properties [2], temperature [3], pressure [4], and so on. A marked effect of the external conditions on the structures of Cu^{II} coordination compounds can also be observed on the cation $Cu(H_2O)_6{}^{2+}$, which appears in the mutually isomorphous Tutton salts, $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$; this is distorted to different extents [5–9], depending on the nature of the cation M^I. The different distortion degrees of the coordination polyhedra of copper in these salts showed up distinctly in the electronic [10] and ESR [11] spectra of these compounds.

One of our previous papers [12] demonstrated that the structures of the coordination polyhedra strongly influence the course of thermal decomposition of Cu^{II} coordination compounds. Thermal analysis even allows one to register differences in the chemical behaviour of distortion isomers of Cu^{II} complexes [13]. It therefore appeared interesting to investigate to what degree the differences in the tetragonal distortion of Cu^{II} coordination polyhedra in the compounds $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ influence their thermal decomposition. Papers concerned with the study of the thermal decomposition of coordination compounds consider one of the significant factors influencing the courses of thermal decomposition to be the nature of the outer-sphere ions [14, 15]. Their influence becomes evident if it is considered that the ionic size, its charge and the electronic configuration of the outermost two electronic shells affect the strengths of electrostatic interactions in the crystal lattice, and thus they have a considerable effect on the total energy content of the system.

In the complexes under investigation, a change in M^I also causes a change in the distortion degree of the coordination polyhedron in the $Cu(H_2O)_6^{2+}$ cation. The question arises as to whether it is the change in the strengths of the electrostatic interactions, or that in the distortion degree of Cu^{II} coordination polyhedron, which determines the course of thermal decomposition of these compounds. In order to answer this question, complexes $M^I_2Ni(SO_4)_2 \cdot 6\,H_2O$ were also investigated, containing the same cations M^I as the copper(II) complexes. The two series of compounds are isomorphous, and thus possible differences in the courses of their thermal decomposition can not be assigned only to different crystal structures. At any rate, for complexes of Ni^{II} as central atom, with the d^8 electronic configuration, manifestation of the Jahn-Teller effect cannot be expected, and neither can marked structural deviations of the $Ni(H_2O)_6^{2+}$ cation from the regular octahedral arrangement.

Experimental

Chemicals. $CuSO_4 \cdot 5\,H_2O$ recrystallized, $NiSO_4 \cdot 7\,H_2O$, $(NH_4)_2SO_4$, K_2SO_4, Tl_2SO_4, all p.a. (Lachema, Brno); Rb_2SO_4 p.a. (Serva, Internat. Chemie- u. Handels-GmbH and Co., Heidelberg).

Syntheses. The complexes investigated were prepared according to the methods presented in [16, 17].

Analytical methods. Copper(II) and nickel(II) contents in the prepared compounds were determined complexometrically against murexide indicator, while the water content was ascertained from the thermal decomposition curves. The analytical compositions of the studied complexes are shown in Table 1.

Table 1

Analytical compositions of the prepared complex compounds

Complex	% Cu		% H_2O	
$M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ M^I =	calc.	found	calc.	found
NH_4	15.89	15.84	27.03	27.20
K	14.38	14.44	24.46	25.00
Rb	11.88	11.88	20.21	20.80
Tl	8.63	8.62	14.68	14.00
$M^I_2Ni(SO_4)_2 \cdot 6\,H_2O$	% Ni		% H_2O	
NH_4	14.86	14.80	27.34	27.50
K	13.43	13.50	24.71	24.72
Rb	11.08	11.00	21.00	20.38
Tl	7.65	7.58	14.50	14.08

Apparatus. The thermal decomposition of the complexes was studied with an OD 102 derivatograph (MOM Budapest). Platinum crucibles with an upper diameter of 14 mm were used. Temperature was measured with Pt-Pt,Rh thermocouples, and the investigations were made in an air atmosphere. To test suitable experimental conditions, samples of 200 and 100 mg were used and the rate of temperature increase was 6, 3 and 1.5°/min.

Thermogravimetric curves were also obtained using a Mettler thermobalance, in a dynamic nitrogen atmosphere with a flow rate of 7 dm^3/h. The sample weight was 7 mg, and the heating rate 6°/min.

Before measurements, all samples were sieved to a mesh size of 0.05. The ΔH values for the studied reactions were obtained by means of a Perkin-Elmer DSC-1B calorimeter calibrated to the melting heat of pure indium. Samples of 1.5–3 mg were placed in aluminium dishes with holes in their lids, allowing the volatile products to escape. The reaction course was studied in the temperature range 293–400 K at a temperature increase rate of 8°/min.

Determination of E^* and ΔH values. For the calculation of experimental activation energy values the Coats–Redfern method was applied[18]. The experimental results were evaluated using the least squares method. A reaction order of one appeared to be the most convenient for all reactions studied. The effect of the experimental conditions on the E^* values was investigated for the compound $(NH_4)_2Cu(SO_4)_2 \cdot 6\,H_2O$. The results obtained (Table 2) indicate that the E^* values depend comparatively little on the measuring conditions, the deviations from the average value being less than $\pm 6\%$. Analogous results were also obtained for the other complexes. Therefore, the experimental conditions subsequently used for the measurements were as follows: sample weight 100 mg, temperature increase rate 3°/min. The E^* values listed in Tables 2 and 3 were obtained as the averages of at least five measurements.

The ΔH value was computed via the relation

$$\Delta H = A \cdot K_a \cdot m^{-1}$$

where A is the area defined by the deflection on the DSC record, K_a is the calibration constant of the apparatus and m is the sample weight.

Table 2

Effects of the experimental conditions on the values of E^* for the dehydration of $(NH_4)_2Cu(SO_4)_2 \cdot 6\,H_2O$

Sample, mg	Heating rate, deg.min^{-1}	E^* kJ · mol^{-1}	r	n
200	6	95.2	0.999	1
200	3	102.0	0.999	1
200	1.5	105.6	0.988	1
100	3	103.5	0.999	1
7	6	98.9	0.998	1

Results and discussion

On heating, the complexes $M_2^ICu(SO_4)_2 \cdot 6\,H_2O$ undergo decomposition in the way described in [16]: four water moles per mole of the complex escape in the first step, while in the second decomposition step the remaining two moles of water are set free. Analogously as for the starting compounds, the intermediates of the thermal decomposition of the Cu^{II} complexes under investigation are also mutually isomorphous [19, 20]. For $M_2^INi(SO_4)_2 \cdot 6\,H_2O$ the same stoichiometry of thermal decomposition was found as for the Cu^{II} complexes [18], but according to [19, 20] those complexes decompose in one step only to form $M_2^INi(SO_4)_2$. Further, under the experimental conditions used in the present study, all six water molecules bonded in $M_2^INi(SO_4)_2 \cdot 6\,H_2O$ were released in one step. Thus, it is apparent that, although the studied compounds of Cu^{II} and Ni^{II} are mutually isomorphous and contain the same cations in their outer spheres, the stoichiometries of their thermal decompositions are different. A comparison of the structures of $(NH_4)_2Cu(SO_4)_2 \cdot$ $\cdot\, 6\,H_2O$ [5] and $(NH_4)_2Ni(SO_4)_2 \cdot 6\,H_2O$ [21], for example, shows that in both compounds all water molecules are hydrogen-bonded to two sulphate groups, and the difference actually consists only in the degree of distortion of the octahedra, that of $Cu(H_2O)_6{}^{2+}$ being more distorted than that of $Ni(H_2O)_6^{2+}$. However, the stoichiometries of decomposition of the two compounds cannot be directly correlated with the interatomic distances between the central atom and the oxygen. Based on the Ni – O bond lengths in the cation $Ni(H_2O)_6{}^{2+}$, it should logically be expected that complexes with these cations will first lose the two water molecules coordinated to the central atom by longer bonds. In the compound $(NH_4)_2Cu(SO_4)_2 \cdot 6\,H_2O$ the three pairs of water molecules exhibit bonds of different lengths to the central atom [5]. With this compound too, however, the assumption did not hold that in the first step of thermal decomposition only two water molecules, bonded to the central atom by the weakest bondings, will become free. The experimental results do not agree with the quantum-chemical computations according to which the water molecules coordinated with the longest bonds should be substituted first in the discrete ions $[Cu(H_2O)_6]^{2+}$ [22]. With regard to the fact that the structures of Cu^{II} coordination compounds may also be affected by increased temperature [3, 23], we investigated whether the complexes in the present study undergo structural changes during the increase of temperature, but before the decomposition point is reached. DSC records of the compounds before dehydration did not show any enthalpy changes measurable under the experimental conditions used; this fact is in accordance with the results obtained for $(NH_4)_2Cu\,(SO_4)_2 \cdot 6\,H_2O$ [24]. Powder diffraction patterns of the studied Cu^{II} complexes exhibit a great number of diffraction lines, and some temperature-induced changes in them are difficult to evaluate. It can not be said from our experimental results whether structural changes other than a temperature-caused expansion of the crystal structure also occur before decomposition. The given course of thermal decomposition of complexes $M_2^ICu(SO_4)_2 \cdot 6\,H_2O$ and $M_2^INi(SO_4)_2 \cdot 6\,H_2O$ is probably due to the instability of the assumed first decomposition intermediate, which would still have four water molecules coordinated to the central atom. For Ni^{II} complexes an instability of the intermediate containing two water molecules is also suggested, though this can be prepared under other experimental conditions [18].

With respect to the stated stoichiometry of thermal decomposition of the complexes $M^I_2M^{II}(SO_4)_2 \cdot 6\,H_2O$ and also to the aims of the present study, we obtained values of E^* and ΔH for the reactions

$$M^I_2Cu(SO_4)_2 \cdot 6\,H_2O(s) \rightarrow M^I_2Cu(SO_4)_2 \cdot 2\,H_2O(s) + 4\,H_2O(g) \qquad (1)$$

$$M^I_2Cu(SO_4)_2 \cdot 6\,H_2O(s) \rightarrow M^I_2Ni(SO_4)_2(s) + 6\,H_2O(g) \qquad (2)$$

where $M^I = NH_4$, K, Rb and Tl.

The obtained values of the experimental activation energies for both complex series (Table 3) indicate that the outer-sphere cations do not affect the courses of thermal decomposition of the Cu^{II} and Ni^{II} complexes in the same manner. Therefore, it is concluded that the increase in the E^* values for the series of Cu^{II} complexes is connected with the change in the distortion degree of the Cu^{II} coordination polyhedron in the $Cu(H_2O)_6{}^{2+}$ cation, rather than with the change in the electrostatic interactions in the crystal structure caused by the change of the ionic radius and the electronic configuration of the M^I cations. With increasing degree of tetragonal distortion of the $Cu(H_2O)_6{}^{2+}$ cation, the lengths of the Cu – O bonds in the axial positions (R_L) also increase, while those in the equatorial plane (R_{S1} and R_{S2}) become shorter (Table 4) [5–9]. We assume that in the studied reactions the water molecules bonded in the axial positions, as well as those with longer bond lengths in the equatorial plane, split off of the central atom. The remaining lengths fall from NH_4^+ to Tl^+. It seems, therefore, that the shortening of the Cu – O bonds in the equatorial plane affects the activation energy value more than does the elongation of the same bonds in the axial direction. Justification of the presented conceptions of the relationship between the structures of the $Cu(H_2O)_6{}^{2+}$ cations and the experimental values of the activation energy is also supported by the fact that

Table 3

Values of E^* for dehydration of the complexes $M^I_2M^{II}(SO_4)_2 \cdot 6\,H_2O$

$M^I_2Cu(SO_4)_2 \cdot 6H_2O$ $M^I =$	T^*	E^* kJ · mol^{-1}	$M^I_2Ni(SO_4)_2 \cdot 6\,H_2O$ $M^I =$	E^*, kJ · mol^{-1}
NH_4	0.905	100.0 ± 4.6	NH_4	102.1 ± 5.0
K	0.881	105.2 ± 3.2	K	111.2 ± 5.0
Rb	0.864	112.0 ± 3.7	Rb	105.0 ± 5.0
Tl	0.858	138.5 ± 0.5	Tl	97.1 ± 5.0

* T (tetragonality degree) $= \dfrac{R_{S1} + R_{S2}}{2\,R_L}$

See also Table 4

Table 4

Internuclear Cu — O distances in the complexes $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ [5–9]

M^I in $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$	NH_4	K	R	Tl
R_{S1} [pm]	207.25	206.9	203.1	201.7
R_{S2} [pm]	196.60	194.3	195.7	195.7
R_L [pm]	223.00	227.8	230.2	231.7

in the Ni^{II} complex series with the same outer-sphere cations the observed dependence of the E^* values on cation M^I was not analogous with that for the Cu^{II} complexes. On the contrary: on passing from the NH_4 to the Tl^+ salt, the values of E^* weakly decrease. However, the authors of [25] found a different order for the E^* values for both complex series. The main differences between the present results and those found in [25] are shown in the E^* values for the decompositions of $Rb_2Cu(SO_4)_2 \cdot 6\,H_2O$ and $Tl_2Cu(SO_4)_2 \cdot 6\,H_2O$, while the remaining values are numerically near.

The ΔH values obtained for reactions (1) and (2) are listed in Table 5. At first it appears surprising that these values for the copper(II) complexes depend comparatively little on the degree of distortion of the Cu^{II} coordination polyhedron in the $Cu(H_2O)_6{}^{2+}$ cation. However, with consideration to the total energetic state of the $Cu(H_2O)_6^{2+}$ cation in the presence of various outer-sphere cations, we came to the conclusion that, due to the plasticity of the coordination sphere of the Cu^{II} the total energy contents in all the systems become very near one another. The same consideration may be applied to the products of the reactions studied, *viz.* the compounds $M^I_2Cu(SO_4)_2 \cdot 2\,H_2O$. The small differences in the ΔH values for reaction (1) in the presence of various cations M^I can be explained by the fact that the energetic states of the starting compounds and those of the reaction products are very near. The highest value of ΔH in the series of Cu^{II} complexes was found for the ammonium salt, indicating its somewhat peculiar position. Indeed, the $Cu(H_2O)_6{}^{2+}$

Table 5

Values of enthalpy changes in the decomposition of the complexes $M^I_2M^{II}(SO_4)_2 \cdot 6\,H_2O$ (M^{II} = Cu, Ni)

$M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ M^I =	ΔH, kJ · mol^{-1}	$M^I_2Ni(SO_4)_2 \cdot 6\,H_2O$ M^I =	ΔH, kJ · mol^{-1}
NH_4	78.5	NH_4	108.0
K	63.1	K	96.4
Rb	65.6	Rb	117.0
Tl	66.0	Tl	67.0

cations in the crystal structure of this compound are differently oriented with respect to the sulphate groups and M^I cations as compared with the other compounds of this series, so that the coordination polyhedron of Cu^{II} may also be considered as a flattened tetragonal bipyramid.

In the Ni^{II} complex series the ΔH values do not change uniformly with the ionic radius of M^I. For the ammonium and rubidium salts they were found to be higher than the activation energy values. Since the reactions discussed are endothermic, it is assumed that the dehydration of the nickel(II) salts is not a simple one-step process.

In conclusion, we would like to emphasize that a comparison of the results obtained for the isomorphous series of Cu^{II} and Ni^{II} compounds led to the finding that the course of thermal decomposition of the Cu^{II} coordination compounds was affected more by the distortion degree of the coordination polyhedron than by outer-sphere cations. The change in the distortion degree of the $Cu(H_2O)_6^{2+}$ cation influenced the values of the experimental activation energy rather than those of ΔH.

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Résumé — On a étudié la décomposition thermique des complexes $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ et $M^I_2Ni(SO_4)_2\,.\,6\,H_2O$ ($M^I = NH_4$, K, Rb, Tl) contenant le cation complexe $[M^{II}(H_2O)_6]^{2+}$ (M^{II} = Cu, Ni). On a établi que les valeurs E^* de l'énergie d'activation experimentale des réactions de déshydratation des deux cations étaient influencées de façon différente par les cations de la sphère extérieure présents.

On est donc arrivé à la conclusion que l'énergie d'activation de la décomposition de $[Cu(H_2O)_6]^{2+}$ dépend du degré de déformation tetragonale de ce cation qui augmente avec le rayon ionique du cation M^I. Les valeurs de ΔH des réactions étudiées dépendent moins de la structure des polyèdres de coordination.

Zusammenfassung — Untersucht wurde die thermische Zersetzung der Komplexe $M^I_2Cu(SO_4)_2 \cdot 6\,H_2O$ und $M^I_2Ni(SO_4)_2 \cdot 6\,H_2O$ ($M^I = NH_4$, K, Rb, Tl), die das komplexe Kation $[M^{II}(H_2O)_6]^{2+}$ enthalten. Die für Dehydratationsreaktionen beider komplexen Kationen ermittelten Werte von E^* bei der thermischen Zersetzung von Kupfer(II)- und Nickel(II)-Komplexen zeigen eine durch Kationen der äußeren Sphäre unterschiedliche Beeinflussung. Daraus wird gefolgert, daß die Aktivationsenergie der Zersetzung von $[Cu(H_2O)_6]^{2+}$ vom Grad der tetragonalen Verzerrung dieses Kations abhängt, der mit wachsendem Ionenradius des Kations M^I steigt. Mit wachsender tetragonalen Verzerrung des Kations $[Cu(H_2O)_6]^{2+}$ steigt auch der Wert der experimentellen Aktivationsenergie. Die Abhängigkeit der ΔH-Werte der untersuchten Reaktionen von der Struktur des Koordinationspolyeders ist geringer.

Резюме — Изучено термическое разложение комплексов $M^I_2Cu(SO_4)_2 \cdot 6H_2O$ и $M^I_2Ni(SO_4)_2 \cdot 6H_2O$ ($M^I = NH_4$, K, Rb, Tl), содержащих сложный катион $[M^{II}(H_2O)_6]^{2+}$ (M^{II} = Cu, Ni). Значения экспериментальной энергии активации, полученной для реакций дегидратации обоих катионов, различным образом зависят от наличия внешне-сферного катиона. Сделано заключение, что энергия активации разложения $[Cu(H_2O)_6]^{2+}$ зависит от степени тетрагонального нарушения этого катиона, увеличивающегося с ионным радиусом катиона M^I. Значения ΔH изученных реакций в меньшей степени зависимы от структуры координационного полиэдра.