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THE RELATIONSHIP BETWEEN THE STRUCTURE OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS: VI.

Thermal decompositions of some pentacoordinated aqua complexes of Cu(II) with heterogeneous spheres

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Data on the activation energies of dehydration of the complexes $[Cu(en)_2(H_2O)]X_2$, $[Cu(\alpha,\alpha'\text{-bipy})_2(H_2O)]S_2O_6$ and $[Cu(o\text{-phen})_2(H_2O)]X_2$ were gained by means of dynamic TG, and the ΔH values of the same reactions by DSC. The results were correlated with known data on the crystal structures of the studied complexes. No significant differences between E and/or ΔH values were found for tetragonal pyramidal and trigonal bipyramidal complexes. For complexes with sufficiently exactly solved crystal structures, the activation energies increase with decreasing values of the anisotropic temperature factors (in the $Cu{-}OH_2$ bond directions). Activation energy values are also influenced by the type of structural changes accompanying the formation of the intermediate of thermal decomposition.

In previous papers [1–3] it was shown that the course of thermal decomposition of hexacoordinated Cu(II) complexes with homogeneous and heterogeneous coordination spheres distinctly depend on the structural parameters (static as well as dynamic) of their coordination polyhedra. In the chemistry of Cu(II) coordination compounds, great interest is nowadays paid to compounds involving coordination number 5. These can exist in the form of a trigonal bipyramid or a tetragonal pyramid, and the questions of their mutual interchange [4] and of energetic differences between them [5] are especially interesting.

The thermal decompositions of the complexes

$[Cu(en)_2(H_2O)][Cu_2(CN)_4]^a$ (1)
$[Cu(en)_2(H_2O)][Cu_2(SeCN)(CN)_3]$ (2)
$[Cu(en)_2(H_2O)][Ni(edta)] \cdot 3\,H_2O^b$ (3)
$[Cu(en)_2(H_2O)][Ni(edta)]$ (3a)
$[Cu(bipy)_2(H_2O)]S_2O_6{}^c$ (4)
$[Cu(o\text{-phen})_2(H_2O)](BF_4)_2{}^d$ (5)
$[Cu(o\text{-phen})_2(H_2O)](NO_3)_2$ (6)

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were studied in this work. [a] en = ethylenediamine, [b] edta = anion of ethylenediaminetetraacetic acid, [c] bipy = α, α′-bipyridine, [d] *o*-phen = 1,10-phenanthroline.

The goal was to establish whether it is possible to find differences in activation energy and decomposition enthalpy between complexes with tetragonal pyramidal structures (complexes 1–3a) and those with trigonal bipyramidal structures (complexes 4–6) in their coordination polyhedra. We also wanted to obtain further information on the correlation between the structural features of the coordination polyhedra and the course of their thermal decomposition.

Experimental

Chemicals

$CuSO_4 \cdot 5 H_2O$, $Cu(NO_3)_2 \cdot 3 H_2O$, $Cu(BF_4)_2 \cdot 6 H_2O$, all p.a. grade; $CuCO_3 \cdot \cdot Cu(OH)_2 \cdot n H_2O$, purum; $NiCO_3 \cdot 2 Ni(OH)_2 \cdot 4 H_2O$, p.a. Ethylenediamine (LaChema Brno) was freshly distilled before use; *o*-phenanthroline and α,α′-bipyridine, both p.a. grade, were used without further purification. $BaS_2O_6 \cdot 2 H_2O$ was prepared according to [6].

Synthesis

All complexes were prepared according to known procedures: complex (1) according to [7]; complex (3) according to [8]; complex (3a) by isothermal dehydration of (3) at ≈ 130°; complexes (5) and (6) according to [9, 10]; and complex (4) according to [11]. Complex (2) was obtained from the authors of [12].

Analytical methods

The C, N and H contents of the prepared complexes were found by elemental analysis on an automatic analyser (Carlo Erba, Milano). Results are given in Table 1.

Table 1 The analytical compositions of the prepared complexes

Complex	% C		% N		% H	
	calc.	found	calc.	found	calc.	found
1	22.20	21.30	25.88	25.75	4.19	4.17
2	18.79	18.27	21.90	21.63	3.55	3.22
3	27.71	27.33	13.85	13.72	5.98	5.94
4	43.55	43.36	10.11	10.31	3.27	3.31
5	46.78	46.96	9.10	9.08	2.94	2.56
6	50.88	50.84	14.84	14.71	3.20	3.24

Instruments and measuring methods

The thermal decompositions of the studied complexes were carried out on an OD 102 derivatograph (MOM, Budapest). 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 200 mg, and the heating was 3 deg min^{-1}. Before measurements, all samples were finely powdered and sieved to a mesh size of 0.018. The thermogravimetric curves of some samples were also obtained on a Perkin—Elmer TGS-1 thermobalance, with a sample weight of ≈ 5 mg and a heating rate of 5 deg min^{-1}. All these experiments were performed in air atmosphere. The values of activation energies E were gained from thermogravimetric curves using the Coats—Redfern method [13]. For evaluation, the least-squares method was used, the reaction order being chosen from five values (0, 1/3, 1/2, 2/3 and 1) according to the criterion of best linearity.

The ΔH values for the studied reactions were obtained by means of a Perkin—Elmer DSC-2 calorimeter, calibrated to the melting heat of pure indium. Samples of ≈ 3 mg were placed in aluminium dishes with holes in their lids, allowing the volatile products to escape. The rate of temperature increase was 8 deg min^{-1}. The evaluation of DSC curves was performed on a table computer, connected to the calorimeter.

Electronic spectra of the studied complexes and of the intermediates of their thermal decomposition were run on a Perkin—Elmer 450 spectrophotometer, using the nujol technique.

Results and discussion

A. The course of dehydration of tetragonal pyramidal complexes

This group of complexes includes the compounds containing the cation $[Cu(en)_2(H_2O)]^{2+}$. Their coordination polyhedron is formed by four nitrogen atoms from two ethylenediamine molecules. These form the approximately square planar base of the pyramid, with the water molecule in the axial position. The anions $[Cu_2(CN)_4]^{2-}$ [7] and $[Cu_2(SeCN)(CN)_3]^{2-}$ [12] form polymeric three-dimensional networks, with the cations $[Cu(en)_2(H_2O)]^{2+}$ in the cavities. In the complex (3), the cation $[Cu(en)_2(H_2O)]^{2+}$ is also bonded to one carboxylic oxygen atom from $Ni(edta)^{2-}$ [8]. The coordination polyhedron of Cu(II) in this complex is therefore better described as a tetragonal bipyramid, similarly as in the complexes $[Cu(en)_2(H_2O)]X_2$ ($X = Cl^-, Br^-$) [14, 15].

All complexes discussed in this section, with the exception of (3), lose the coordinated water molecule in the first step of their thermal decomposition (Table 2). From complex (3), three water molecules escape in the first step of thermal decomposition, and one molecule of water in the second step (Table 2). All products of dehydration are sufficiently thermally stable to be prepared and studied.

Table 2 Data on the thermal decompositions of square pyramidal complexes

Complex	Reaction	T_d, °C	Weight loss, % calc.	found
1	$-H_2O$	115	4.16	4.2
2	$-H_2O$	105	3.52	3.8
3	$-3H_2O$	95	8.90	9.0
3a	$-H_2O$	70	3.26	3.3

On the basis of the stoichiometry of the thermal decomposition of (3), it was presumed that the three non-coordinated water molecules escape in the first decomposition step, and the coordinated water molecule is evolved only in the second decomposition step. We tried to prove this assumption. The electronic spectra of complexes (3) and (3a) are equal in the visible region, with the maximum of the *d–d* absorption band at 17 800 cm^{-1}. The electronic spectrum, however, did not change after the total dehydration of this complex. The assumption that (3a) contains a coordinated molecule of water is confirmed by the IR spectra of (3) and (3a). Both exhibit the absorption band with maximum at ≈ 880 cm^{-1} which is typical of coordinated water molecules [15]. From the electronic and IR spectra, it can be stated that the coordination polyhedron of Cu(II) in this complex is practically unchanged during the first step of its thermal decomposition.

The values of activation energy E^* and reaction enthalpy ΔH for the studied square pyramidal complexes are given in Table 3, together with the interatomic distances $Cu—OH_2$ and the maxima of the *d–d* absorption bands of the initial complexes and of the intermediates formed in the dehydration reactions. The activation energy for complex (3a) was obtained from two kinds of measurements. In the first one, the TG curves of the complex prepared by isothermal decomposition of (3) were evaluated; in the second kind of measurements (E^* values in brackets), the E^* value was cal-

Table 3 Some thermal, structural and spectral data on the studied square pyramidal complexes

Complex	E^*, kJ mol^{-1}	ΔH, kJ mol^{-1}	r(Cu—O), nm	Maximum of *d–d* abs. band, · 10^3 cm^{-1} I	II
1	75±7	58±2	0.2441 [a]	18.35	18.4
2	83 [b]	31 [b]	0.2331 [c]	18.2	—
3	78±10	—	water of cryst.	17.75	17.8
3a	48±4	57±3	0.2632 [d]	17.8	17.8
	(43±5)	(39±2)			

[a] ref. [7]; [b] results gained from one measurement only; [c] ref. [12]; [d] ref. [8]; I — maximum of *d–d* transition band of original complex, II — maximum of *d–d* transition band of decomposition reaction product.

culated from the TG curve of the original complex (3). The differences between the two E values lie within the experimental error. We concluded that the mode of complex preparation did not play such a role as in the case of $CuSO_4 \cdot H_2O$ [16], for example, which means that no further structural changes take place before the dehydration of $[Cu(en)_2(H_2O)][Ni(edta)]$. However, it is of interest that the activation energy of dehydration of complex (3) is higher than the activation energy of dehydration of (3a). The crystal water molecules escape at lower temperature, but with higher activation energy than the coordinated water molecule. After the loss of the crystal water molecules, the whole complex is destabilized, as manifested in the decomposition temperature and in the values of E^* and ΔH.

The spectral data (Table 3) indicate that the electronic structures of the Cu(II) coordination polyhedra were nearly unaffected by the dehydration. It may be concluded that the water molecules in the original complexes are only weakly coordinated, and during the dehydration no noteworthy substitution reaction takes place. The relatively low activation energy and ΔH values found for these complexes could be connected with this structural situation.

The E^* values found for the tetragonal pyramidal complexes discussed in this work are lower than those for $Cu(en)_2(H_2O)X_2$ ($X = Cl^-$, Br^-) [3]. However, these complexes possess deformed tetragonal bipyramidal structures, and the originally outersphere halide atom replaces the lost water molecule.

B. The course of dehydration of trigonal bipyramidal complexes

The second group of studied complexes contains Cu(II) aqua complexes with CuN_4O chromophore, but with trigonal bipyramidal structures of their coordination polyhedra: $[Cu(bipy)_2(H_2O)]S_2O_6$ (4), $[Cu(phen)_2(H_2O)](BF_4)_2$ (5) and $[Cu(phen)_2(H_2O)](NO_3)_2$ (6). The water molecule in these complexes is coordinated to Cu(II) in the equatorial plane. The interatomic distances $Cu-OH_2$ are shorter than in square pyramidal complexes, but within the given polyhedron they form the long bonds again. All the studied complexes lose the molecule of water in the first step of their thermal decomposition (Table 4). The products of dehydration are again thermally stable enough to be prepared and studied.

The intermediate of thermal decomposition of complexes (5) and (6) were prepared by isothermal dehydration. These complexes contain 1,10-phenanthroline as N-ligand. It is assumed [17] that this ligand unlike 2,2′-bipyridyl, does not form tetracoordinated, deformed tetrahedral coordination polyhedra with Cu(II). From the electronic spectra of the dehydrated products of complexes (5) and (6) (Table 5), it may be presumed that after dehydration complex (6) is still trigonal bipyramidal, the water molecule probably being replaced by the nitrate group. However, a *cis*-octahedral or bicapped square pyramidal structure, as in $[Cu(bipy)_2(NO_3)]NO_3 \cdot H_2O$ [18], cannot be excluded.

The electronic spectrum of dehydrated complex (5), with the appearance of two *d–d* transition bands of nearly equal intensity, suggests a quite changed structural

Table 4 Data on the thermal decompositions of trigonal bipyramidal complexes

Complex	Reaction	T_d, °C	Weight loss, % calc.	Weight loss, % found
4	$-H_2O$	135	3.25	3.3
5	$-H_2O$	51	2.92	2.8
6	$-H_2O$	102	3.20	3.2

Table 5 Some thermal, structural and spectral data on the studied trigonal bipyramidal complexes of Cu(II)

Complex	E^*, kJ mol^{-1}	ΔH, kJ mol^{-1}	$\Delta U^{1/2}$	r(Cu–OH$_2$), nm	Maximum of d–d abs. band, · 10^3 cm^{-1} I^a	II
4	76±10	52±3	0.036	0.2158^a	12.45	–
5	83±2 (100±4)	32±3	0.022	0.2235^b	13.4	16.2 14.4
6	166±12 (174±12)	51±2	0.026	0.2183^c	12.5	13.1

I – complex before, II – complex after dehydration; [a] ref. [11]; [b] ref. [9]; [c] ref. [10].

situation (Table 5). This spectrum resembles that of Cu(bipy)$_2$(PF$_6$)$_2$ [17]. The coordination polyhedron in this complex has a deformed tetrahedral structure [19]. The complex Cu(phen)$_2$(BF$_4$)$_2$ can also be prepared in monocrystal form. The crystal structure solution is in progress and will be published later, together with further details on the IR and ESR spectra.

The activation energies and ΔH values for the decompositions of these complexes (Table 5) did not differ significantly from those found for complexes (1)–(3a), though the Cu–OH$_2$ bond lengths are quite different in these two groups of complexes.

The Cu–OH$_2$ bond vector in complexes (4)–(6) is practically parallel to the crystallographic b axis and the half-axes of the thermal ellipsoids of the Cu and O atoms are also nearly parallel to crystallographic axes. It was possible in these cases, therefore, to evaluate the relationship between the E^* values and the values of $\Delta U_{ii}^{1/2}$ [20], where $\Delta U_{ii}^{1/2}$ is the square root of the difference between the U values of the oxygen and copper atoms in the bond direction: $\Delta U_{ii}^{1/2} = [U_{ii}(O) - U_{ii}(Cu)]$. It was found that for complexes (4) and (5) (Table 5) E^* increases with decreasing $\Delta U^{1/2}$. The E^* value found from derivatographic measurements on complex (6) was relatively very high and did not agree with the $\Delta U_{ii}^{1/2}$ value sequence for this series of complexes. This is why the E^* values for (5) and (6) were also found from measurements on "microsamples" (values given in brackets in Table 5). These values are somewhat different, but they did not alter the trend of the activation energy changes in this group of complexes. The discrepancy between the E^* and $\Delta U^{1/2}$ values for complex (6) may be caused by the very low exactness of its crystal structure solution (with $R = 11.8\%$).

On the basis of the data obtained in this work, it may be stated again that the activation energy values are not affected by the absolute value of the length of the cleaved bond, but much more so by the overall energetic state of the coordination polyhedron, which may be expressed by the $\Delta U^{1/2}$ values. The values of ΔH are less affected by the coordination polyhedron structures than was observed with the E^* values. However, the ΔH values for the dehydration of complexes (2) and (5) are very low, and we are not yet in a position to explain this.

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Zusammenfassung — Werte für die Aktivierungsenergien bzw. ΔH-Werte der Dehydratisierung der Komplexe $[Cu(en)_2(H_2O)]X_2$, $[Cu(\alpha,\alpha'\text{-bipy})_2(H_2O)]S_2O_6$ und $[Cu(o\text{-phen})_2(H_2O)]$ wurden durch dynamische TG bzw. DSC erhalten. Die Ergebnisse wurden mit bekannten Daten über die Kristallstruktur der untersuchten Komplexe verglichen. Keine signifikanten Unterschiede zwischen E^*- und/oder ΔH-Werten wurden für tetragonal-pyramidale und trigonal-bipyramidale Komplexe gefunden. Die Untersuchung von Komplexen mit genügend genau bekannter Kristallstruktur hat ergeben, daß die Aktivierungsenergie mit abnehmenden Werten des anisotropen Temperaturfaktors (in der Cu—OH_2-Bindungsrichtung) abnimmt. Die Aktivierungsenergie wird auch durch den Typ der die Bildung von intermediären thermischen Zersetzungsprodukten begleitenden strukturellen Veränderungen beeinflußt.

Резюме — С помощью динамической ТГ и ДСК были получены энергии активации и ΔH реакций дегидратации комплексов [Cu(этилендиамин)$_2$(H_2O)]X_2, [Cu(α,α'-бипиридил)$_2$(H_2O)]S_2O_6 и [Cu(*o*-фенантролин)$_2$(H_2O)]X_2. Полученные результаты коррелировались с кристаллоструктурными данными комплексов. В случае тетрагонально-пирамидальных и тригонально-бипирамидальных комплексов не наблюдалось значительного различия в величинах E и ΔH. Для комплексов с точно определенными кристаллическими структурами энергии активации увеличиваются с уменьшением значения анизотропного температурного фактора в направлении связей Cu—OH_2. Значение энергии активации также зависит от типа структурных превращений, вызывающих образование промежуточного продукта в реакциях термического разложения.