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THE ROLE OF COORDINATION POLYHEDRON GEOMETRY AND ITS STRUCTURAL CHANGES IN THE DEHYDRATION KINETICS OF $[Cu(\widehat{LL})_2(H_2O)]X_2$ COMPLEXES

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ABSTRACT

Thermal decomposition of tetragonal-pyramidal and trigonal-bipyramidal pentacoordinated Cu(II) complexes was studied. Kinetic studies of $[Cu(\widehat{LL})_2(H_2O)]X_2$ type complexes dehydration showed that the activation energies found for release of water molecule from apical position in tetragonal pyramid are somewhat lower than those, found for splitting of water molecule from equatorial position in trigonal bipyramid. These differences can be explained considering slightly different stabilities of both coordination polyhedra types, and the structural changes of Cu(II) coordination polyhedra, occuring during their dehydration.

INTRODUCTION

The study of the influence of Cu(II) coordination polyhedra structure on the course of thermal decomposition of coordination compounds showed that at Cu(II) complexes with coordination number six the activation energies of decomposition reactions were influenced by the deformation degree of coordination polyhedra [1]. However, further study showed that this criterion does not reflect the energetical state of decomposed particles wholly, and other structural factors may be of importance, also.[2]. Among these structural factors the values of anisotropic thermal parameters of ligands' donor atoms seem to be significant [2]. It was, anyway, of interest to find out, whether more pronounced differences in the structures of Cu(II) coordination polyhedra will be reflected in the activation energies of decomposition reactions. Therefore we have studied complexes $[Cu(\widehat{LL})_2(H_2O)]X_2$, where $\widehat{LL}$ is chelating ligand, coordinated to Cu(II) through nitrogen atoms, such as ethylenediamine (en), 2, 2 - bipyridyl (bpy) and 1,10-phenantroline (phen). Complexes, containing en as $\widehat{LL}$ ligand have tetragonal-pyramidal structure with water molecule coordinated in apical position. Complexes with bpy and

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phen as $\widehat{LL}$ have trigonal-bipyramidal structure with water molecule coordinated in equatorial plane.At the same time it was of interest to study the structural changes, accompanying the dehydration and their possible role in the decomposition kinetics.

EXPERIMENTAL PART

The studied complexes were prepared according to known procedures. Their dehydrated forms were prepared by heating them on the decomposition temperature of parrent $[Cu(\widehat{LL})_2(H_2O)]X_2$. Composition of all prepared samples was controlled analytically. Infrared and electronic spectra were measured in nujoll mulls on the Specord IR-75 (400-4 000 cm^{-1}) and Unicam SP 700 (6 000 - 30 000 cm^{-1}) Thermal decomposition was performed on Derivatograph OD 102. Before measurements all samples were finely powdered and sieved to a mesh size of 0.018. The activation energies were calculated from at least 5 TG curves according to [3], using the least-squares procedure.

RESULTS AND DISCUSSION

In tetragonal-pyramidal $[Cu(en)_2(H_2O)]X_2$ complexes vary the apical Cu - OH_2 bond distances in relatively large interval (Table 1). All of them are considerably longer than Cu - N bond distances. The relatively low values of activation energies for reactions

$$[Cu(\widehat{LL})_2(H_2)]X_{2(s)} \longrightarrow Cu(\widehat{LL})_2X_{2(s)} + H_2O_{(g)}$$

(where $\widehat{LL}$ = en) reflect probably the fact that water molecules are coordinated very "loosely". As a consequence of this, the coordination polyhedra structures remain during the decomposition nearly without change (Table 3). However, the low experimental activation energies are rather surprising, because the outer-sphere anions form three-dimensional network, the $Cu(en)_2(H_2O)^{2+}$ cations being placed into its cavities.

Complexes $[Cu(\widehat{LL})_2(H_2O)]X_2$ with trigonal-bipyramidal structures of coordination polyhedra ($\widehat{LL}$ = bpy and phen) have the water molecules coordinated in equatorial planes. Again are the bond distances Cu - OH_2 longer than Cu - N distances, however the difference between them is expressively lower ,than at previously discussed tetragonal-pyramidal complexes. The activation energies, gained for dehydration of these complexes are somewhat higher (Table 2) than those, found for tetragonal-pyramidal complexes. This can be connected with the slightly higher stability of the trigonal-bipyra-

Table 1. Some structural and thermal data on tetragonal-pyramidal $[Cu(en)_2(H_2O)]X_2$ complexes

Complex X/2	E^* $kJ\ mol^{-1}$	S^* $J\ mol^{-1}K^{-1}$	T_d ^{o}C	r(Cu-O) nm	Ref.
$Cu_2(CN)_4^{2-}$	75 ± 7	- 13 ± 2	115	0.2441	4
$Cu_2(SeCN)(CN)_3^{2-}$	83	-10	105	0.2331	5
$Ni(edta)\cdot 3\ H_2O$	78 ± 10	- 12 ± 3	95	crys.H_2O	6
$Ni(edta)^{2-}$	43 ± 5	- 22 ± 5	70	0.2632	6

midal structure in comparison with the teragonal-pyramidal one [10], as well as with more pronounced structural changes of coordination polyhedra during the thermal decomposition of trigonal-bipyramidal complexes, clearly reflected in the electronic spectra of dehydrated compounds (Table 3). The most pronounced structural changes of coor-

Table 2. Some structural and thermal data on trigonal-bipyramidal $[Cu(\widehat{LL})_2(H_2O)]X_2$ complexes

Complex	E^* $kJ\ mol^{-1}$	S^* $J\ mol^{-1}K^{-1}$	T_d ^{o}C	r(Cu-O) nm	Ref.
$[Cu(bpy)_2(H_2O)](S_2O_6)$	76 ± 10	- 15 ± 3	135	0.2158	7
$[Cu(phen)_2(H_2O)](BF_4)_2$	100 ± 4	- 6 ± 1	51	0.2235	8
$[Cu(phen)_2(H_2O)](NO_3)_2$	166 ± 12		102	0.2183	9

dination polyhedron were registered at $[Cu(phen)_2(H_2O)](BF_4)_2$ decomposition. The originally trigonal-bipyramidal polyhedron was changed into a deformated tetrahedral structure of coordination polyhedron without coordination of BF_4^-. The other two trigonal-bipyramidal complexes retain according to their electronic spectra, their original structure, the water melecules being replaced by outer-sphere anion. Anyway, it seems that the fact,whether the counter anion is during the thermal decomposition coordinated or not, does not influence the activation energy values.

The comparison of the gained activation energy values with the

Table 3. Spectral data on $[Cu(\widehat{LL})_2(H_2O)]X_2$ and $Cu(\widehat{LL})_2X_2$ complexes

Complex	Maximum of d-d absorption bands, cm^{-1} Hydrated complexes	Dehydrated complexes
$[Cu(en)_2(H_2O)]X_2$		
X/2 =		
$Cu_2(CN)_4^{2-}$	18 350	18 400
$Ni(edta)^{2-}$	17 750	17 800
$[Cu(bpy)_2(H_2O)](S_2O_6)$	12 450	12 600
$[Cu(phen)_2(H_2O)](BF_4)_2$	13 400	15 600 14 400
$[Cu(phen)_2(H_2O)](NO_3)_2$	12 500	13 300 10 700

splitted bonds $Cu-OH_2$ lengths (Table 1 and 2) show that there exist no simple correlation between these two sets of data. This may be considered as further evidence of the assumption that for the decomposition kinetics is the overall energetical state of the decomposed complex more important than the splitt-of ligands´bond length.

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