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

XVI. Thermal dehydration of some pentacoordinate aquacarboxylato Cu(II) complexes

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Abstract

The thermal dehydration of pentacoordinate complexes [Cu(maleinate)(H_2O)] (I), [Cu_2(citrate)(H_2O)$_2$] (II) and [Cu(phenoxyacetate)$_2$(H_2O)$_3$] (III) was investigated and correlated with the structural changes occurring during the dehydration. It was found that the activation parameters of the reactions do not follow the lengths of the split Cu–OH_2 bonds. The lowest E_a and lg$A$ values were found for compound I, the highest ones for compound III. The most expressive changes of the anionic ligand binding mode take place during the dehydration of this compound.

Keywords: chemical transformation, complexes, kinetics, pentacoordinate aquacarboxylato Cu(II) complexes

Introduction

Pentacoordinate Cu^{II} compounds with heterogeneous coordination sphere are more frequent than those with homogeneous coordination sphere. In this contribution we do want to examine the thermal behaviour of copper(II) aquacarboxylates with chromophores CuO_4O', CuO_3O_2' and CuO_2O_3' as they occur in Cu(maleinate)·H_2O [1], Cu_2(citrate)·$2H_2O$ [2] and Cu(phenoxyacetate)$_2$·$3H_2O$ [3] with respect to their structures.

Experimental

Syntheses and chemical analysis

The compounds [Cu(maleinate)(H_2O)] and [Cu(phenoxyacetate)$_2$(H_2O)$_3$] were crystallized from solutions gained by the solution of freshly prepared

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$Cu(OH)_2$ in warm water solution of the corresponding acids after filtering off the unsoluted $Cu(OH)_2$. The compound $[Cu_2(citrate)(H_2O)_2]$ was prepared from water solution of $CuCl_2{\cdot}2H_2O$, citric acid and urea according to [2]. The intermediates and products of thermal dehydration of studied compounds were prepared via regulated thermal decomposition of the starting hydrates. The chemical composition of the gained compounds was checked by chemical analysis. The content of Cu was found by complexometric titration (indicator murexid), that of C and H by elemental analysis (Carlo Erba, Milano) and the content of water was established thermogravimetrically (Table 1).

Thermal decomposition of compounds under study was followed using derivatograph OD 102 in air atmosphere. Platinum crucibles with upper diameter of 14 mm were used, temperature was measured by Pt-Pt, Rh thermocouples, heating rate 2.5 deg$\cdot$min^{-1}, reference material α-Al_2O_3, sample mass 200 mg. Before measurements, all samples were finely powdered and sieved to a mesh size 0.18–0.15.

X-ray powder patterns of the compounds were gained on the Czechoslovak goniometer GON-2 with CuK_α radiation and Ni filter.

Infrared spectra were taken on Specord 75-IR spectrophotometer in the region 400–1700 cm^{-1}, the electronic spectra were measured on Specord M-40 between 11.000 and 35.000 cm^{-1}. Both types of measurements were done using nujol suspension technique.

Evaluation of the kinetic parameters for the studied reactions were done from the TG curves using Coats-Redfern [4] and Skvára-Sesták methods [5]. For the method [4] least squares procedure was used, the reaction order *n* was choosen from 5 values (0, 1/3, 1/2, 2/3 and 1) according to the criterion of the best linearity. All given activation parameters are the mean values of at least 5 measurements.

Results and discussion

All complexes under study exhibit pentacoordination of central atom, the coordination polyhedron being distorted tetragonal pyramid in maleinate and phenoxyacetate compounds [1, 2] and trigonally distorted tetragonal bypiramid in citrate compound [3]. However considerable differences were found [1–3] concerning the mode of carboxylate anions coordination and their possibilities to substitute the evolved water molecules. While the maleinate anion in the $[Cu(maleinate)(H_2O)]$ does not have further possibilities to coordinate and its rigid binding mode [1] in the reactant does not allow any serious changes under dehydration, the citrate and phenoxyacetate anions do possess several further possibilities for coordination.

Thermal decomposition of compound [Cu(maleinate)(H_2O)] (Table 2) starts at 90°C and proceeds in one step. Low values of E_a and A calculated for this reaction indicate that there doesn't occure any expressive changes of the crystal structure. In this case, however the Cu(II) coordination polyhedron has to change to a square-planar shape. Electronic spectra of the hydrated and dehydrated compounds are very different, the symmetric *d-d* transition band centered at 14.500 cm^{-1} with a badly resolved shoulder at ca. 12.000 cm^{-1} for the hydrated compound being changed to a spectrum containing two intensive, badly resolved absorption bands at 16.000 and 14.200 cm^{-1} after dehydration. This type of electronic spectrum for a Cu^{II} compound is believed [6] to indicate it's square-planar coordination.

Dehydration of [Cu_2(citrate)(H_2O)$_2$] (Table 2) starts at 40°C and for this reaction again relatively low values of E_a and lg$A$ were found. Dehydration proceeds in one step, according to the TG and DTG curve. Because both water molecules are bonded to one central atom at very different distances (Table 2) is this finding in agreement with statement [7] that the course of thermal decomposition doesn't reflect the spacings central atom-leaving ligand in all cases. However, the position of the hydrogen atoms in the compound coudn't be identified without doubt, and a possibility of a proton transfer to the bridging OH group was not excluded [3]. The coordination polyhedron of Cu^{II} can be regarded as tetragonal-pyramid with strong trigonal distorsion [2], the apical water molecule being more far from Cu^{II} atoms. The coordination polyhedron of the Cu^{II} atom can be also regarded as a distorted trigonal bipyramid with both water molecules in the equatorial plane. The water molecule, which form longer bond to this Cu^{II} atom forms also bridge to the second, crystallographically unequivalent Cu^{II} atom. The dehydration of this compound is reversible and is not connected with expressive changes in its crystal structure (Table 3). In the IR spectrum of dehydrated compound only the libration water vibration disappeared with respect to the IR spectrum of hydrated compound. The ν_{as}(COO) and ν_s(COO) at 1440 and 1340, 1360 cm^{-1} are identical in the spectra of both compounds. The differences in the electronic spectra of both compounds are small, as well. The hydrated compound exhibit one *d-d* transition, centered at 13.100 cm^{-1}, the dehydrated one at 12.900 cm^{-1} and a shoulder at 17.200–17.500 cm^{-1} on the charge transfer band.

The dehydration of [Cu(phenoxyacetate)$_2$(H_2O)$_3$] starts at room temperature, and it is connected with highest E_a and A values from among the studied compounds (Table 2). We have investigated only the first decomposition step, in which one from the water molecules is split and the [Cu(phenoxyacetate)$_2$(H_2O)$_2$] is formed. The structure of [Cu(phenoxyacetate)$_2$(H_2O)$_3$] [3] consist from isolated tetragonal pyramids, being held in the sheets by hydrogen bonds (Table 4). The access to the sixth coordination place is blocked by unco-

Table 1 Analytical composition of the compounds under study

Compound	MW / $g \cdot mol^{-1}$	Cu / %		C / %		H / %		H_2O / %	
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
Cu(mal)·H_2O	195.57	32.58	32.49	24.30	24.54	2.25	2.06	9.5	9.2
Cu(mal)	177.56	35.65	35.79	26.92	27.03	1.25	1.14		
Cu_2(citr)·$2H_2O$	351.20	36.00	36.18	20.81	20.50	2.11	2.29	20.0	20.0
Cu_2(citr)	315.17	40.68	40.32	21.47	22.84	2.29	1.28		
Cu(phenac)·$3H_2O$	419.65	14.90	15.14	50.85	50.27	4.19	4.18	8.5	8.9
Cu(phenac)·$2H_2O$	401.68	15.87	15.81	46.05	45.75	5.00	4.80	12.0	12.0

Abbreviation: mal=maleinate dianion, citr= citrate tetraanion, phenac= phenacetate anion

Table 2 Data on structures and thermal decomposition of studied complexes

Compound	Structure data	Thermal decomposition			
	d(Cu–OH_2) /Å	Decomp. scheme	T_d /°C	E_a /$kJ \cdot mol^{-1}$	lg$A$
Cu(mal)·H_2O	2.262 [1]	–H_2O	90	66.8±2.5	5.4*
				60.6±1.8	5.0^+
Cu(citr)·$2H_2O$	2.096 [2]	–$2H_2O$	40	80.6±2.0	9.1*
	2.284			74.9±4.0	7.4^+
Cu(phenac)$_2$·$3H_2O$	2.02, 2.03	–H_2O	22	82.8±2.5	13.4*
	2.27 [3]			89.5±3.0	11.9^+

Abbreviation: mal=maleinate dianion, citr= citrate tetraanion, phenac= phenacetate anion
* data calculated according to [4], $^+$data calculated according to [5]

ordinated carboxylic oxygen atoms from two phenoxyacetate groups. There is no possibility of hydrogen bonds formation between the sheets. In the compound [Cu(phenoxyacetate)$_2$(H$_2$O)$_2$] the Cu^{II} atom is hexacoordinated [8], two new coordination bonds being formed to the etheric oxygen atoms in spite of the fact that uncoordinate carboxylic oxygen atoms are in favorable position in the reactant. The phenoxyacetato group has to be rotated around the Cu–O(carboxyl) bond, to come in positions suitable for its coordination through etheric oxygen atoms in the axial positions. We suppose that these changes are only possible after loosening of hydrogen bonds network and they are favored ener-

Table 3 X-ray powder diffractograms of [Cu$_2$(citr)(H$_2$O)$_2$] and of [Cu$_2$(citrate)]

[Cu$_2$(citr)(H$_2$O)$_2$]			[Cu$_2$(citrate)]		
2θ	d / Å	I_r	2θ	d / Å	I_r
12.2	7.25	33	12.2	7.25	26
			12.5	7.10	31
15.7	5.64	100	15.7	5.64	51
			16.5	5.37	26
			17.1	5.18	100
18.2	4.82	10			
19.2	4.62	50			
19.7	4.50	27	19.7	4.50	35
			22.1	4.02	39
23.2	3.83	33			
24.6	3.62	11	24.4	3.65	52
25.3	3.52	5	25.7	3.46	21
26.2	3.39	18			
28.2	3.16	17			
28.8	3.09	16	29.1	3.04	29
29.6	3.02	12			
30.5	2.93	15	30.4	2.94	13
31.0	2.88	11	31.3	2.85	11
			33.3	2.65	15
33.9	2.53	9			
			35.7	2.51	16
			37.0	2.43	20

getically due to the 5-member ring formation instead of sterically stresses 4-member ring, which would be formed due to carboxylic oxygen atom coordination.

Table 4 X-ray powder patterns of $[\mathrm{Cu(phenoxyacetate)_2(H_2O)_3}]$ and $[\mathrm{Cu(phenoxyacetate)_2(H_2O)_2}]$

$[\mathrm{Cu(phenoxyacetate)_2(H_2O)_3}]$			$[\mathrm{Cu(phenoxyacetate)_2(H_2O)_2}]$		
2θ	d / Å	I_r	2θ	d / Å	I_r
6.1	14.48	100	6.1	14.48	100
7.4	11.94	18			
10.4	8.50	5	10.2	8.66	6
10.6	8.36	8	107	8.26	18
10.8	8.18	13			
			12.1	7.31	4
15.8	5.6	5	15.9	5.57	5
17.1	5.18	14	17.1	5.18	14
18.1	4.90	16			
20.4	4.35	10	20.0	4.44	18
			20.7	4.29	7
21.4	4.15	10	21.4	4.15	22
23.2	3.83	11			
23.6	3.77	8	23.5	3.78	12
			25.2	3.53	5
27.1	3.29	5	27.2	3.28	10
28.1	3.17	5			

Concluding, we can say that the activation parameters E_a and A found for the dehydration reactions are not the greater the shorter are the split-off Cu–OH$_2$ bonds. The overall changes of the reactant's structure are the factors dominating the reaction course and it's quantitative parameters.

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Zusammenfassung — Die thermische Dehydratation der pentakoordinativen Komplexe [Cu(Maleinat)(H_2O)] (I), [Cu_2(Zitrat)(H_2O)$_2$] (II) und [Cu(Phenoxyacetat)$_2$(H_2O)$_3$] (III) wurde untersucht und mit den Strukturveränderungen bei der Dehydratation in Korrelation gestellt. Man fand, daß sich die Aktivierungsparameter der Reaktion nicht nach der Länge der Cu–OH_2 Bindungen richten. Der niedrigste E_a- und lg$A$-Wert ergab sich für die Verbindung I, der höchste für die Verbindung III. Die ausgeprägtesten Änderungen der Art der anionischen Ligandenbindung erfolgen bei der Dehydratation dieser Verbindung.