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THE INFLUENCE OF THE STRUCTURE AND COMPOSITION OF COMPLEXES OF THE TYPE CuA_2X_2 ON THE COURSES OF THEIR THERMAL DECOMPOSITION

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The influence of different degrees of distortion of the coordination polyhedra in some Cu(II) complexes on the courses of their thermal destruction was studied. It was found that differences in the thermal stability and stoichiometry of thermal decomposition may be satisfactorily explained by the different degrees of distortion of the coordination polyhedra in the Cu(II) complexes under discussion. This fact appears to be significant with respect to the chemical reactivities of these complexes, though the influence of other factors cannot be excluded.

The recent development of science is characterized by an explosive evolution of experimental techniques, allowing one to obtain very precise data on the structures of substances. Due to these possibilities, a new type of isomerism has been detected for copper(II) complex compounds [1], called distortion isomerism [2]. The existence of this type of isomerism is well explained by the theory of vibronic interactions in electronically degenerated states of the central atom [3]. This theory, together with a number of experimental data [3], pointed to the marked plasticity of the coordination sphere of Cu(II), a consequence of which is the occurrence of Cu(II) complexes not in one but in several possible stable conformations differing in the lengths of their Cu – ligand bonds [3]. At present distortion isomers are called substances with the same stoichiometric composition, but with different degrees of distortion of their coordination polyhedra. As follows from the definition, the differences in the stuctures of distortion isomers are smaller, than those of the classical types of isomers, e.g. cis-trans isomers. The structural differences between distortion isomers may be determined not only by monocrystal X-ray analysis, but also by a number of other physicochemical methods allowing the study of structures of substances (IR, electronic, EPR spectra, etc.).

It is clear that chemists will not only be interested in the static determination of differences in the complex compounds under investigation: their interest will be directed mainly to the chemical behaviour of the compounds. One of the

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possibilities for studying this problem is given by thermal analysis. This paper has the object of showing to what extent the degree of distortion of the coordination polyhedron influences the course of thermal decomposition.

Discussion

The study of complexes of $CuCl_2$ with alkyl derivatives of ammonia [4] showed for compounds of the type $CuCl_2L_4$ and $CuCl_2L_2$ that the degree of distortion of the coordination polyhedron increases with increasing σ-donor ability of the ligands and simultaneously as the steric requirements of the ligands advance. A comparison of the data listed in Table 1 leads to the conclusion that with increasing degree of distortion of the coordination polyhedron from L = methylamine through ethylamine to diethylamine (shown in Table 1 by the shift of the maximum of the *d-d* absorption band to higher wavenumbers), the thermal stability of the complex decreases, the evaluation being made on the basis of the decomposition temperature or the maximum of the first endothermic deviation [5]. The temperature at which the reduction of Cu(II) to Cu(I) takes place in the same order decreases. From the results of non-isothermal studies of the decomposition of the complexes listed in Table 1, it may be stated that with an appreciable change of the distortion of the coordination polyhedron (transition from differently distorted tetragonal bipyramide in the case of the complexes $CuCl_2(ma)_2$ and $CuCl_2(ea)_2$ to the practically square-planar structure of $CuCl_2(dea)_2$) a change in the decomposition stoichiometry also takes place. The decompositions of complexes with methyl- and ethylamine as ligands may be expressed in accordance with the results obtained by isothermal methods for ethyl- and diethylamine, respectively, [6–8] by the equations

Table 1

Some thermal and spectral properties of $CuCl_2L_4$ and $CuCl_2L_2$ complexes [5]

Complex	pK_B	Maximum of the 1st endoreaction, °C	$\tilde{\nu}_{max}$ of the $d \to d$ transition, cm^{-1}	Temperature of the Cu(II) reduction, °C
$CuCl_2(ma)_4$	3.37	75	16 400	160
$CuCl_2(ea)_4$	3.22	65	17 300	147
$CuCl_2(ma)_2$	3.37	140	14 000	162
$CuCl_2(ea)_2$	3.22	130	15 300	150
$CuCl_2(dea)_2$	2.89	(100)	18 800 14 800	130

$$CuCl_2L_{2(s)} \rightarrow CuCl_2L_{(s)} + L_{(g)}$$
$$CuCl_2L_{(s)} \rightarrow CuCl + \text{oxidation and polymerization products of } L$$

In contrast to the above complexes, the complex $CuCl_2(dea)_2$ undergoes redox changes simultaneously with the release of first part of the dea [5]. These results are contradictory to the usual opinion of an enhancement of the thermal stability of a complex with increasing basicity of the ligand L. The same dependences were also observed for a series of complexes $Cu(SCN)_2L_2$ [9] and $Cu(OCN)_2L_2$ [10], where L denotes pyridine and its mono- and dimethyl derivatives (Tables 2 and 3). The authors of these papers [9, 10] came to the conclusion that the thermal stability of the studied complexes is most influenced by the steric properties of the ligands. They showed that the influence of a methyl group in the α-position to the donor nitrogen atom is particularly marked, and they suggest that such a methyl group hinders effective interaction of the central atom with the anion ligand leading to the formation of tetragonal-bipyramidal coordination polyhedra.

Table 2

Some thermal and spectral properties of $Cu(NCS)_2L_2$ complexes [9]

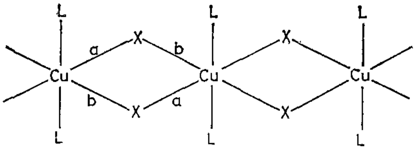
Complex $Cu(NCS)_2L_2$ with L =	pK_B	$\tilde{\nu}_{max}$ of the $d \rightarrow d$ transition, cm^{-1}	Decomposition temperature of the complex, °C
pyridine	8.78	15 600	110
α-picoline	8.04	13 000 16 600	60
β-picoline	8.37	17 100	110
γ-picoline	8.02	16 200	110
2,3-lutidine	7.43	14 100	70
2,4-lutidine	7.37	17 150	65
2,6-lutidine	7.28	14 500 16 700 19 700	65
3,4-lutidine	7.54	13 100 16 300	100
3,5-lutidine	7.85	13 200 16 300	100

Table 3

Some thermal and spectral properties of complexes $Cu(NCO)_2L_2$ [10]

Complex $Cu(NCO)_2L_2$ with L =	pK_B	$\tilde{\nu}_{max}$ of the $d \rightarrow d$ transition, cm^{-1}	Initial decomposition temperature of the complex, °C
α-picoline	8.04	14 800 17 700	80
β-picoline	8.37	15 500	130
γ-picoline	8.02	16 300	155
2,4-lutidine	7.37	13 700 17 100	100
2,6-lutidine	7.28	14 300 16 700 19 300	130

An evaluation of the above data and also a comparison of the literature information on the structure of the complexes CuA_4X_2, CuA_2X_2, $CuAX_2$ and CuX_2 [11 – 13] with their thermal stabilities [14, 15] permits the conclusion that the thermal stability of a Cu(II) complex is markedly enhanced by the formation of chains. It may be stated that the less symmetrical the chain, i.e. the more different the values of *a* and *b*, the lower the thermal stability of the copper(II) complex.



Based on the infrared, electron and EPR spectra [4], in the complex $CuCl_2(ma)_2$ a pseudooctahedral structure is suggested, in which the lengths of the Cu – X bonds may be considered to be equal; on the change to ethylamine ligands the structure becomes a distorted tetragonal bipyramid [4], the Cu – X_2 – Cu – chain becomes asymmetrical; owing to this, the distribution of the electron shell between the involved atoms changes, with weakening of the bond Cu – L, the ethylamine molecule being released more easily from the complex than the methylamine molecule. The complex compound $CuCl_2(dea)_2$ exhibits a square-planar structure [4, 16] (as the complexes CuN_4^{2+}), and owing to this its thermal stability decreases appreciably.

The situation appears to be more complicated for the group of complexes $Cu(NCS)_2L_2$ and $Cu(NCO)_2L_2$, where dative π-bonds between the central atom and the ligand L and the group NCX (X = 0, S) are also to be considered. Nevertheless, in general it holds that the thermal stability of a complex is the lower, the more distorted the coordination polyhedron, i.e. the more the structure approaches the square-planar form. An exception is the complex $Cu(NCO)_2$(2,6-lutidine$_2$), where an optimum balance of the factors influencing the stability of the system (steric effect, formation of dative π-bonds and crystal lattice energy) is suggested [10].

The foregoing showed that the differences in thermal stability of the complexies CuX_2A_2 (at least for the discussed series) may be satisfactorily explained by the different degrees of distortion of the coordination polyhedra, though of course, other factors must also be taken into consideration.

The following part of this paper will deal with the different degrees of distortion of the coordination polyhedra of Cu(II) in compounds with the same stoichiometric composition, *viz.* in distortion isomers, demonstrated by the courses of their thermal decomposition.

In evaluating the data of the behaviour of distortion isomers of copper(II) complexes during their thermal decomposition, we may divide the observed differences into two groups.

I. Differences in the decomposition temperature. In evaluating these differences, it is necessary to decide whether they are really caused by different interactions in the inner coordination polyhedra, or between the coordination polyhedra, or only by physical effects (e.g. defects of the crystal lattice, particle size, transport phenomena, etc.).

Table 4 presents the temperature of decomposition, that of the maximum of the first deviation on the DTA curve, the values of the valence vibrations for the bond between the central atom and the nitrogen of the neutral ligand and the frequencies of the absorption band maxima of the *d-d* transitions in the electronic spectra of the complexes, for some pairs of distortion isomers.

Table 4

Some thermal and spectral properties of some couples of distortion isomers

Complex	T_d, °C	T_M, °C	$\tilde{\nu}_{Cu-N}$, cm^{-1}	$\tilde{\nu}_{max}$ $d \to d$ trans. $\cdot 10^3$cm^{-1}	References
α-$CuBr_2(NH_3)_2$	110	293	482, 416	14.8	1, 17, 18
β-$CuBr_2(NH_3)_2$	140	289	491, 418	14.1	1, 17, 18
α-$CuCl_2(py)_2$	122	200	265	14.8	19
β-$CuCl_2(py)_2$	138	210	268	14.6	19
α-$CuCl_2(\gamma$-pic$)_2$	135	164	296	14.7	19
β-$CuCl_2(\gamma$-pic$)_2$	145	184	300	14.8	19
α-$Cu(NCS)_2(py)_2$	110	185	258, 220	15.6	20
β-$Cu(NCS)_2(py)_2$	110	175	253, 218	—	20
α-$Cu(HCOO)_2(NH_3)_2$	130	135	460, 430	15.6	21
β-$Cu(HCOO)_2(NH_3)_2$	137	142	460, 432	15.9	21, 22
α-$Cu(C_2O_4)(NH_3)_2$	182	226	488	15.4	23–26
β-$Cu(C_2O_4)(NH_3)_2$	187	218	480	15.6	23–26
γ-$Cu(C_2O_4)(NH_3)_2$	193	229	488	15.7	23–26

A comparison of the values of the decomposition temperature (T_d) and of $\tilde{\nu}_{Cu-N}$ shows that the dependence existing between them is not simple. For the majority of the isomer pairs observed the increase of the decomposition temperature of one of the isomers is in accordance with the greater strength of the metal – ligand bond. The difference in the values of the valence vibration $\tilde{\nu}_{Cu-N}$ for α- and β-$Cu(NCS)_2py_2$ did not influence the decomposition temperature, but on the other hand for α- and β-$Cu(HCOO)_2(NH_3)_2$ the difference in T_d amounted to 7°, though the value of $\tilde{\nu}_{Cu-N}$ was the same for both complexes. The fact that the decomposition temperatures do not change equally with changes in $\tilde{\nu}_{Cu-N}$ in all the cases is ascribed to different interactions between the coordination polyhedra.

An evaluation of the above information leads us to the conclusion that the values of the temperature of decomposition and also of the maxima of the corresponding deviations in the DTA curves reflect the differences in the distortion of the coordination polyhedra as well as those of the strength of the Cu – volatile ligand bond, but their numerical values are of course influenced by other interactions too.

In comparing the decomposition temperatures of, for example, the α-isomers of the studied pairs, it is clear that these temperatures are strongly influenced by other factors in addition to the metal – volatile ligand bond strength. The lowest decomposition temperature in the compared series is exhibited by $\alpha\text{-CuBr}_2 \cdot (NH_3)_2$, while of the studied anions Br^- shows the weakest ability to form hydrogen bridges.

It is sometimes preferred in the literature to evaluate the strength of the ligand coordination by means of the maximum temperature (T_M) of the corresponding deviation in the DTA curve [27]. The data listed in Table 1 show that the differences in the strength of the ligand coordination given by the value of $\tilde{\nu}_{Cu-N}$ also appear in the values of T_M. However, it is not possible here either simply to compare T_M with $\tilde{\nu}_{Cu-N}$.

II. The second group of significant differences in the courses of thermal decomposition of distortion isomers of Cu(II) complexes covers those of the decomposition stoichiometry. For complexes of the composition CuX_2A_2, where X denotes anions consisting of several atoms, their infrared spectra, and in some cases also the results of their X-ray structure analysis, indicate differences in the coordination of the polyatomic anions to the central atom. These complexes showed differences in their decomposition stoichiometry. Though one cannot suppose that no changes of the bonding conditions occur in the solid residues during the first phases of thermal decomposition, it seems that in these cases the stoichiometry of thermal decomposition is influenced significantly by the structure of the starting complex. The isomers of $Cu(NCS)_2(py)_2$ may be considered as an example [20]. The decomposition of $\beta\text{-}Cu(NCS)_2(py)_2$ is the same as shown in [28] and takes place with the formation of CuSCN · SCN; the α-form yields a compound of the same composition but of different structure only if the decomposition proceeds in a nitrogen flow. With decomposition in air, the isolated intermediate has the composition $Cu_2S(CN)_2S_2(CN)_2$ [20]. The different course of thermal destruction in the region of decomposition of the thiocyanate groups is in good agreement with the data of other physico-chemical methods, pointing to the fact that the structural differences between the isomers are due to the different symmetries or positions of the thiocyanate groups in the crystal lattice.

For the isomers of $Cu(NCS)_2(NH_3)_2$ it has been found [29] that in addition to the differences in the bond lengths in the inner coordination polyhedron, those complexes also differ in the angle of deviation of the NCS group from linearity. The DTA curves showed marked differences just in the region where the destruction of the thiocyanate group occurs [30]. The changes in the thermal decomposition of the isomers of $Cu(NCS)_2(NH_3)_2$ when they are exposed to pressure are interesting. The detailed character of the changes due to pressure in the coordination sphere of Cu(II) and in the whole lattice is not perfectly clear, but powder diffractograms, lead us to the suggestion [30] that the changes in the coordination polyhedra probably occur with a mutual shift of some planes in the lattice. The decomposition temperature of the product is lower by about 50° than the original temperature (130°) and according to the TG curve two moles of NH_3 are released in the first step, while only one mole of ammonia is liberated from the original samples [30].

Another example is given by the isomers of $Cu(C_2O_4)(NH_3)_2$, the decomposition of which was studied by calorimetric methods [23]. The first decomposition step of α- and β-$Cu(C_2O_4)(NH_3)_2$ may be expressed by the equation

$$\alpha\text{-}, \beta\text{-}Cu(C_2O_4)(NH_3)_{2(s)} \rightarrow Cu(C_2O_4)(NH_3)_{(s)} + NH_{3(g)}$$

The values of ΔH for this reaction ($\Delta H_\alpha = 10.5$ kcal.mole^{-1} and $\Delta H_\beta = 13.9$ kcal.mole^{-1}) indicate unequal interactions of the ammonia molecules with the central atom and also within the whole crystal lattice. The γ-isomer exhibits quite another situation, since even in the first step of thermal decomposition a considerable decomposition of the oxalate group itself takes place. A different type of bonding of the $C_2O_4^{2-}$ ion and also a different $Cu-NH_3$ interaction in the structures of these complexes have been found by direct X-ray structure analysis [31] as well as by other physico-chemical methods [24–26].

The isomers of $Cu(NH_3)_2(HCOO)_2$ also show different courses of decomposition on heating [22]. According to the TG and DTG curves, the α-isomer decomposes in only one step to Cu, NH_3, H_2O and CO_2, whereas the decomposition of the β-form yields a green intermediate of composition $Cu(NH_3)_{1.5}(HCOO)_2$, this having been considered the β-form itself in the older literature.

Conclusion

The object of this paper was to demonstrate a direct relationship between the structures of Cu(II) coordination compounds, or more exactly between the degrees of distortion of the coordination polyhedra, and the courses of their thermal decomposition. Though, of course, we cannot exclude the influence of physical factors, which in reactions of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$ in general play an important part, nor the effect of secondary interactions within the crystal lattice, nevertheless, on the basis of the presented experimental data we may state that the courses of thermal decomposition of copper(II) complexes (for an analogous or equal stoichiometric composition of the complexes) are strongly affected by the degree of distortion of the coordination polyhedron. With respect to the chemical reactivity of these complexes, this fact appears to be rather significant.

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RÉSUMÉ – On a étudié l'influence des différents degrés de distortion des polyhèdres de coordination sur l'allure de leur décomposition thermique, dans le cas de quelques complexes du Cu(II). On a trouvé que les différences de stabilité thermique et de stoechiométrie pouvaient expliquer de manière satisfaisante les différents degrés de distortion des polyhèdres de coordination dans les complexes du Cu(II) étudiés. Ce fait semble être plutôt significatif de la réactivité chimique de ces complexes, bien que l'influence d'autres facteurs ne doive pas être exclue.

ZUSAMMENFASSUNG — Der Einfluß der verschiedenen Grade der Koordinations-Polyeder-Verzerrung in einigen Cu(II) Komplexen auf den Verlauf ihrer thermischen Zersetzung wurde untersucht. Es wurde festgestellt, daß Unterschiede in der thermischen Stabilität und der Stöchiometrie der thermischen Zersetzung durch die verschiedenen Verzerrungsgrade der Koordinations-Polyeder in den erörterten Cu(II) Komplexen befriedigend erklärt werden können. Diese Tatsache scheint hinsichtlich der chemischen Reaktivität dieser Komplexe von grosser Bedeutung zu sein, obwohl der Einfluß anderer Faktoren nicht ausgeschlossen werden kann.

Резюме — Было изучено влияние различной степени искажения координационного полиэдра в некоторых комплексах Cu(II) на ход их термической деструкции. Найдено, что при обсуждении различий их в термической стабильности и стехиометрии термического разложения, может быть удовлетворительно объяснено на основе различной степени искажения координационного полиэдра в комплексах Cu(II). Этот факт, по-видимому, скорее является существенным по отношению химической реакционноспособности этих комплексов, хотя влияние и других факторов не может быть исключено.