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TEMPERATURE INDUCED STRUCTURAL CHANGES OF Cu(II) AND Ni(II) COMPLEXES AND THEIR THERMAL DECOMPOSITION

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The paper discusses the structural changes of some Cu(II) and Ni(II) complexes during the heating and their influence upon the decomposition stoichiometry. The influence of the interactions inside of coordination polyhedra, bonding and stereochemical properties of the counter ions or molecules are discussed in this connection as well. The expressive influence of the plasticity or rigidity of the Cu(II) and Ni(II) coordination polyhedra, respectively, is emphasized.

Present contribution wants to show that the interactions inside the coordination polyhedra as well as the structural changes coordination polyhedra during the heating are crucial for the course of the decomposition reactions. Two main questions are discussed:

1. The atoms in solid state – are they really immobile? Are there any possibilities for changes in their positions, without phase transitions?
2. Are there activated only split-off bonds during the heating?

These items were studied on the Cu(II) and Ni(II) coordination compounds. The influence of the central atoms upon the course of the thermal decomposition is quite frequently studied, however its interpretation is really scarce. The electronic configuration of copper(II) and nickel(II) atoms differs in one electron, Cu(II) having the configuration $3d^9$ and Ni(II) $3d^8$, respectively. This difference is reflected in the "plasticity" of the Cu(II) coordination sphere and "rigidity" of the Ni(II) coordination sphere [1, 2]. Mentioned properties of the coordination spheres of both central atoms were demonstrated on their hexacoordinated complexes. For Cu(II) compounds with different chromophores nearly continuous change from tetragonal to square-planar geometry was found [1]. The situation is completely different for Ni(II) complexes. The "elongation" of octahedra is

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limited to a relatively narrow interval of axial distances, then the geometry is changed abruptly to a square-planar one [2].

The mentioned items are discussed on some examples of thermal decomposition of Cu(II) complexes with chromophores CuO_6, and CuO_4O_2 and Ni(II) complexes with chromophores NiO_6, NiN_4N_2 and NiN_4X_2.

Results and discussion

Compounds of general formula $M^{I}_{2}[M^{II}(H_2O)_6](EO_4)_2$, where M^{I} were NH_4, K, Rb, Cs and Tl, M^{II} were Cu and Ni, E were S and Se, respectively, are all isostructural, as far their crystal structures are known. The complex cations $[Ni(H_2O)_6]^{2+}$ have nearly octahedral structures [3], cations $[Cu(H_2O)_6]^{2+}$have tetragonal ($M^{I}=Cs$), or rhombic symmetry [4]. Other copper compounds containing the same cations are those with benzenesulphonate, 4-toluenesulphonate and D-10-camphorsulphonate anions, again with tetragonally or rhombically deformed hexaquacopper(II) cations [4]. In both of them the axial bonds Cu - H_2O are considerably longer than the equatorial ones, and the same decomposition stoichiometry could be awaited - namely the release of two water molecules in the first decomposition step. This type of decomposition was however observed only for those Cu(II) complexes with tetragonal $[Cu(H_2O)_6]^{2+}$cations [5, 6]. All compounds with rhombically deformed coordination polyhedra of $[Cu(H_2O)_6]^{2+}$release in the first decomposition step four water molecules [5-7]. This made us to study the structural changes of the compounds during the heating. The powder diffractograms of several studied compounds were taken at the temperature of the dehydration onset in a closed sample holder [5, 6]. No changes relating to their room temperature patterns were registered for compounds with tetragonal coordination polyhedra, however the diffractograms for compounds with rhombic ones were slightly but significantly different. The evaluation of the found differences suggested that during the heating the axial $Cu-OH_2$ distances are shortened, whereas the originally longer pair of equatorial $Cu-OH_2$ bonds becomes longer. It is therefore probable that in the moment of the decomposition four nearly equivalent $Cu-OH_2$ bonds were formed, which would explain the found decomposition stoichiometry for compounds with rhombically deformed coordination polyhedra in cations $[Cu(H_2O)_6]^{2+}$. The dehydration of the corresponding Ni(II) compounds proceeds in one step:

$$M_2^I[Ni(H_2O)_6](EO_4) \rightarrow M_2^INi(EO_4)_2$$

and the structure changes due to the temperature raising are or negligible, or they refer only to a slight changes in the dimensions of the elementar cell [6].

The second question, given in the introduction was studied on the dehydration of two known hydrates of copper(II) formates. There are only two water molecules coordinated to the Cu(II) atom in the $Cu(HCOO)_2 \cdot 4H_2O$ [8]. Considering the decomposition scheme:

$$Cu(HCOO)_2 \cdot 4H_2O \rightarrow Cu(HCOO)_2 \cdot 2H_2O$$

it could be predicted that only the originally uncoordinated water molecules are evolved. However, the structure of the resulting compound contains two different copper atoms, one of them being coordinated through four water molecules and two formato oxygens, the other one through six formato oxygen atoms [9]. Moreover, all $HCOO^-$ groups have in the tetrahydrate anti-anti configuration, whereas in the dihydrate only one half of them have the same configuration, the second one have anti-syn configuration [8, 9]. We conclude therefore that during the decomposition nearly all chemical bonds are newly formed. This mean that the heating leads to the activation of all present chemical bonds and not entirely those, which are split-off in the decomposition reaction [10].

The temperature induced structural changes of Ni(II) compounds are always connected with their thermal decomposition or isomerisation, probably because of the rigidity of the Ni(II) coordination polyhedra.

For the reactions of the type

$$\underset{Oh}{[Ni(H_2O)_2L_4]X_2} \rightarrow \underset{S}{[NiL_4]X_2} \rightarrow \underset{Oh}{[NiL_4X_2]}$$

it was found that the dehydration of the monomeric octahedral (*Oh*) complexes is connected with the transformation to a square-planar (*S*) structure or to a monomeric octahedral structure with coordinated anions. It was shown [11] that with increasing basicity of the ligands *L* (pyridine and its derivatives) and with decreasing coordination ability of the anion X (X^- = Cl, Br, I, ClO_4, BF_4) the probability of the formation of square-planar complexes increases [12].

On the other hand, when the starting complexes have pseudo octahedral structures, e.g. the complexes $[\mathrm{Ni}(q\text{-}\mathrm{Rpy})_2(\mathrm{NCS})_2]$, the positions and nature of the substituents (q and R, respectively) are the most important factors, influencing the structures of the Ni(II) coordination polyhedra in the decomposition reactions products [13-16]. Complexes of this type, with substituent in the 4 or 3 position on the pyridine ring liberate Rpy molecules on heating and form products with the composition $\mathrm{Ni(Rpy)(NCS)_2}$ or $\mathrm{Ni(NCS)_2}$ with a more polymeric octahedral structure. However, the complexes with an alkyl substituent in the 2 position show the configurational change square-planar → more polymeric octahedral [17].

Concluding, we can answer the questions, we have asked in the introduction. We can say that the suggestions on the immobile atoms in the solid state, as well as on the activation of only the split-off bonds can lead to serious mistakes in the interpretation of the experimental results. At the same time the integral redistribution of the bond strengths inside of the coordination polyhedra, connected with the weakening of some and strengthening of other bonds is different for central atoms with different electronic configurations and this fact influences strongly the courses of the decomposition reactions, as well.

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Zusammenfassung — Es werden wärmebedingte Strukturveränderungen einiger Cu(II)- bzw. Ni(II)-Komplexe sowie deren Einfluß auf die Stöchiometrie der Zersetzung beschrieben. In diesem Zusammenhang wird auch ebenso der Einfluß von Wechselwirkungen innerhalb des Koordinationspolyeders sowie von Bindungs- und stereochemischen Eigenschaften der Gegenionen oder -moleküle beleuchtet. Es wird der ausdrucksvolle Einfluß der Plastizität und Härte von Cu(II)- und Ni(II)-Koordinationspolyedern hervorgehoben.