

Special Review

THERMAL PROPERTIES OF SOLID NICKEL(II) COORDINATION COMPOUNDS*

PART A: THE STOICHIOMETRY OF THERMAL DECOMPOSITION

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The paper deals with the chemical and physical factors influencing the stoichiometry of thermal decomposition of solid coordination compounds. Nickel(II) coordination compounds were used as examples: the problem of the relationship between the structure of the initial compound (and of its intermediates) and the stoichiometry of thermal decomposition is discussed; experimental conditions are shown to affect this decomposition, and the conceptions of the apparent and real stoichiometries of thermal decomposition are discussed. The results obtained may have a more general meaning.

Owing to the development of experimental techniques and to the continuously increasing interest in the properties of coordination compounds, a great number of papers dealing with the study of their thermal behaviour have been published [1, 2].

In the interpretation of the experimental results obtained, changes caused by temperature in the properties of coordination compounds are often elucidated in a simplified and sometimes erroneous way. The stoichiometry (step-wise character) of thermal decomposition of coordination compounds is one of the basic items of information of this research, and usually only the TG, DTG and DTA curves are subject to analysis. However, it is necessary adequately to interpret thermoanalytical curves, considering the physical and chemical factors which influence the thermal decomposition, and not to simplify too much the questions of the relationship between thermal decomposition stoichiometry and the structures of solid coordination compounds. Based on the example of nickel(II) complexes (and especially on our own results), it was the aim of this work to point to the said problems and to try to explain them. The choice of these complexes was made due to their suitable thermal behaviour, since in releasing volatile ligands (in the temperature interval 20–300°) the complexes do not show any change in the oxidation degree of Ni(II), though this release may be distinctly observed in the thermoanalytical curves. It must be considered, however, that due to the effect of temperature nickel(II) complexes may undergo different stereochemical changes (square plane, octahedron, tetrahedron, etc.), which can also influence the stoichiometry of their thermal decomposition.

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Experimental methods

In the study of the stoichiometry of thermal decomposition, the usual thermo-analytical methods of TG, DTG and DTA (together with chemical and phase analyses and other techniques) were applied. Structural changes caused by temperature were also investigated by means of spectral (infrared and electronic absorption spectra) and magnetic methods (magnetic moment measurements). With these methods the changes of the bonding character (change of end-bonded NCS groups to bridging-bonded, etc.) were investigated, as well as stereochemical transformations (of the type square planar \rightleftharpoons octahedral, etc.).

Basic qualitative data from thermoanalytical curves and the stoichiometry of thermal decomposition

In the study of the thermal properties of coordination compounds, the starting experimental data are the measured (thermoanalytical) curves of the two most important thermoanalytical methods, *viz.* TG and DTA (and DTG, respectively) from which the following qualitative data are usually deduced [2]:

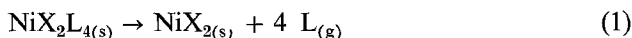
a) The decomposition temperature of the compound under investigation (from the TG, DTG and DTA curves).

b) The stoichiometry of thermal decomposition (number of defined steps, in which volatile ligands escape). DTG curves allow one to distinguish these steps clearly.

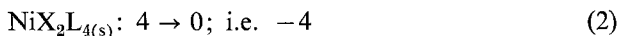
c) Endothermic or exothermic process.

d) Compositions of the intermediates and of the final decomposition products.

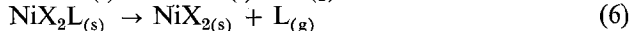
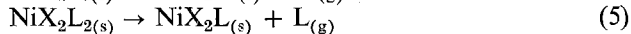
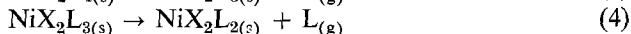
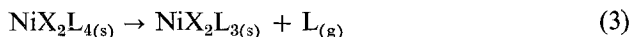
In general the stoichiometry of thermal decomposition of the starting complexes of composition NiX_2L_4 (X = anionic ligand, L = volatile neutral ligand) may take place in one step or it may exhibit several steps. The one-step process means that all volatile ligands L escape in one step, as expressed by the equation:



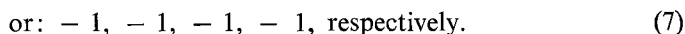
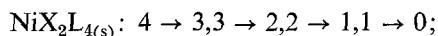
or in a short form:



More often, however, it is a several-step process, when the escape of one or more volatile ligands takes place successively, as expressed by the equations:



or in their short forms:

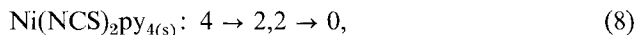


Depending on the nature of the central atom, the ligand properties and the different experimental conditions, some of the expected steps are usually not observed. As regards the solid state of the compound, the influence of the crystal structure also has to be considered; complex species, not occurring in solution can arise in thermal decompositions in the solid phase, and *vice versa*.

The problem of the relationship between the stoichiometry of thermal decomposition and the structure of the initial complex

A different stoichiometry of thermal decomposition of solid coordination compounds, achieved by changing some of the said factors (central atom, ligands, experimental conditions), comprises only one part of the given problem (some of the intermediates according to [3–6] are not always identified). The other part of the question lies in whether it is possible to predict the step-wise course of thermal decomposition reactions by means of structural information on the initial compound [14].

Most nickel(II) coordination compounds with nitrogen heterocyclic ligands are of the type NiX_2L_4 (X = anionic ligand, L = monodentate molecular ligand) and have the molecular structure (NiX_2L_4) . From this group of compounds the complex $\text{Ni}(\text{NCS})_2(\text{pyridine})_4$ was taken as the starting substance, since its stoichiometry of thermal decomposition is known [2]:

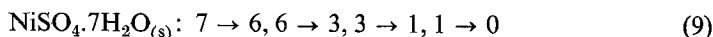


(py = pyridine), and its molecular structure is also known [5]. The four pyridine molecules are in square planar coordination to the Ni(II) atom (the Ni – N(py) internuclear distance being 2.03 Å), and with the two NCS groups form a distorted octahedron (Ni – N(NCS) = 2.12 Å). From the above, however, it does not follow that the two pyridine molecules escaping in the first step ($4 \rightarrow 2$) are less strongly bonded than the other two. Only their infrared spectra, *viz.* the differences in the $\gamma(\text{C} - \text{C})$ and $\gamma(\text{C} - \text{H})$ deformation vibrations of the pyridine molecules (two and two vibrations in the starting complex changed to one and one band in the intermediate) indicated [2] that the four pyridine molecules in the starting complex are not equivalent. Analogously, in the study of the thermal decomposition of the complex $\text{Ni}(\text{NCS})_2(\text{methylamine})_4$ only small differences were found [7] between the coordinated methylamine molecules (two N – H vibrations in the infrared spectra) in spite of the several-step stoichiometry of thermal decomposition. There are fine-structural differences concerning predominantly the region of the secondary coordination sphere (e.g. mutual interactions of structural units in the crystal). For the analysis of the studied relationship, it is necessary to know the whole crystal structure of the starting compound. We therefore oriented our further studies to the thermal decomposition of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, for which these data are known [8]. The types of bonding of the H_2O molecules in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ are listed in Table 1.

Table 1
Bonding possibilities of the H₂O molecules in NiSO₄·7H₂O

| Notation | Number of bonds | Number and type of bonding interaction |
|----------|-----------------|---|
| A | 3 | Ni ^{II} —, SO ₄ ²⁻ < |
| B | 3 | Ni ^{II} —, 2SO ₄ ²⁻ — |
| C | 3 | Ni ^{II} —, 2SO ₄ ²⁻ — |
| D | 3 | Ni ^{II} —, H ₂ O—(F), H ₂ O—(G) |
| E | 4 | Ni ^{II} —, 2SO ₄ ²⁻ —, H ₂ O—(G) |
| F | 4 | Ni ^{II} —, SO ₄ ²⁻ —, H ₂ O—(D), H ₂ O—(G) |
| G | 4 | SO ₄ ²⁻ —, H ₂ O—(D), H ₂ O—(E), H ₂ O—(F) |

The TG curve of NiSO₄·7H₂O shows [9] four identifiable dehydration steps, and its stoichiometry of thermal decomposition may be expressed in the short form:



According to [9] these steps represent the following sequence:

1. Loss of 1/7 of the water molecules, denoted as "A", representing the most weakly bonded;
2. loss of 3/7 of the water molecules ("B, C, D"), breaking three bonds with three different partners;
3. loss of 2/7 of the water molecules ("E, F"), breaking four bonds each; and
4. loss of 1/7 of the water molecules ("G"), breaking four bonds, too.

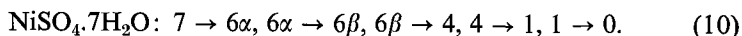
This interpretation cannot be accepted as satisfactory for several reasons:

a) If only the number of bonding interactions is considered, a two-step stoichiometry of thermal decomposition may be expected (7 → 3, 3 → 0).

b) Considering only the types of bonding interactions (6/7 coordinated water molecules and 1/7 lattice water molecules), the stoichiometry of thermal decomposition could exhibit a minimum of two dehydration steps (7 → 1, 1 → 0) and a maximum of six (7 → 6, 6 → 4, 4 → 3, 3 → 2, 2 → 1, 1 → 0).

c) By the escape of 1/7 of the water molecules, the α -modification of NiSO₄·6H₂O is formed, containing the coordination species [Ni(H₂O)₆]²⁺ [8], and thus it has no lattice water molecules at all.

d) In addition, several authors [10–13] support the following stoichiometry of thermal decomposition:



It follows from the above [14] that in searching for correlations between the stoichiometry of thermal decomposition and the structures of solid coordination compounds, it is necessary to analyze every reaction step separately, i.e. the full crystal structures of the intermediates must be known. The structural data on the

starting compound above do not allow prediction of the number of defined intermediates. In addition to the structural factors, transport processes also play an important part (especially the diffusion of volatile ligands), which may cause the formation of a differing number of intermediates, depending on the various experimental conditions.

The influence of various experimental conditions on the stoichiometry of thermal decomposition

Different experimental conditions considerably influence not only the courses of the thermoanalytical curves and the decomposition temperatures, but also the stoichiometry of thermal decomposition (number of defined intermediates). It was due to these factors that for a given complex with a greater number of volatile ligands different authors found different stoichiometries of thermal decomposition. Their results, however, are not always reproducible, because of their insufficient description of the experimental conditions used. A remarkable example from this point of view is the coordination compound $\text{Ni}(\text{NCS})_2(3\text{-methylpyridine})_4(3\text{-methylpyridine} = \beta\text{-picoline})$, for which, depending on the different experimental conditions (Table 2, Fig. 1) different stoichiometries of thermal decomposition were observed [15].

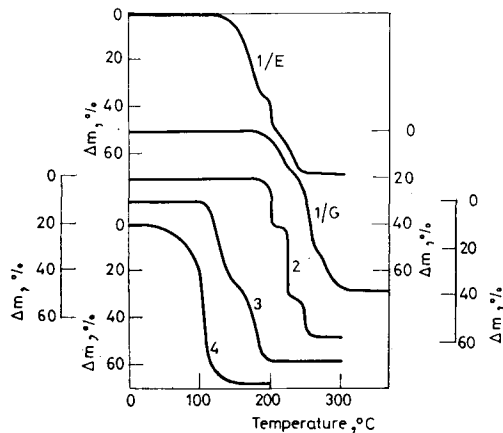


Fig. 1. Decomposition of $\text{Ni}(\text{NCS})_2(\beta\text{-pic})_4$ under various experimental conditions

The starting compound release β -picoline in three steps ($-2, -1, -1$ or $-1, -2, -1$), in two steps ($-2, -2$), or in one step (-4).

It is possible that some of the intermediates are not observed only because, under the given conditions of thermal decomposition, they are thermodynamically unstable. Thermodynamic instability may be shown [15] by an unstable crystal structure of the intermediate, or by an insufficient partial pressure of the ligand

in the gaseous phase. For this latter reason, by decreasing the sample weight, or by working in vacuum, respectively, a lowered number of intermediates may be expected (Table 2). The absence of some intermediates need not be caused

Table 2

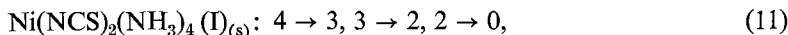
Stoichiometry of thermal decomposition of $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_4$ under different experimental conditions (from TG curves)

| Decomposition | Apparatus | Sample weight, mg | Rate of temperature increase, °/min | Crucible, atmosphere | Stoichiometry of thermal decomposition |
|---------------|-----------------------|-------------------|-------------------------------------|------------------------------|--|
| 1/E | derivatograph | 100 | 3 | platinum, air | -2, -1, -1 |
| 1/G | derivatograph | 500 | 6 | platinum, with a lid, ligand | -1, -2, -1 |
| 2 | derivatograph | 500 | 6 | labyrinth*, ligand | -1, -2, -1 |
| 3 | micro-balance | 2.59 | 0.5 | platinum, air | -2, -2 |
| 4 | vacuum thermo-balance | 10.6 | 2.5 | platinum, vacuum | -4 |

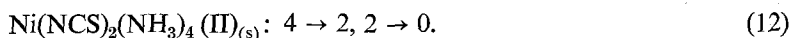
* Measured under quasi-isothermal and quasi-isobaric conditions [16].

by thermodynamic factors only. Nucleation and recrystallization processes of products, which can be influenced by the rate of temperature increase, also play an important part. For an increased rate of sample heating under dynamic conditions of thermal decomposition, only a small number of nuclei of a certain intermediate may occur, so that in the thermal decomposition process this is not recorded in the TG curve; however, it may possibly be identified in the DTG curve and by phase analysis, respectively.

In addition to methodical and instrumental effects in studying the stoichiometry of thermal decomposition of coordination compounds, the physical properties of the samples under investigation (size of the particles, thickness of the layer, mode of sample preparation, etc.) also have to be considered. It has been found [18] that, depending on the conditions of preparation, by crystallization from solution (I) or by heterogeneous reaction of solid $\text{Ni}(\text{NCS})_2$ with gaseous ammonia (II), respectively, complexes of the same composition $\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$ were obtained (after adaptation of the particles to equal sizes); however, these differed in the stoichiometries of their thermal decompositions. Complex I undergoes decomposition in three steps (Fig. 2):



while for complex II the process runs in two steps (Fig. 3):



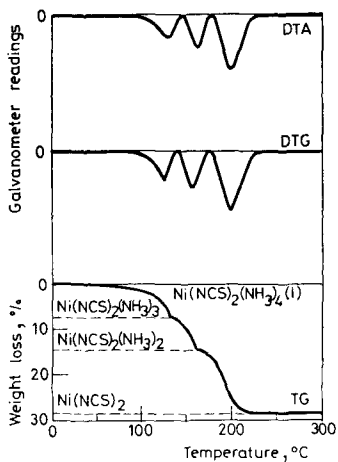


Fig. 2. Thermal curves of complex I

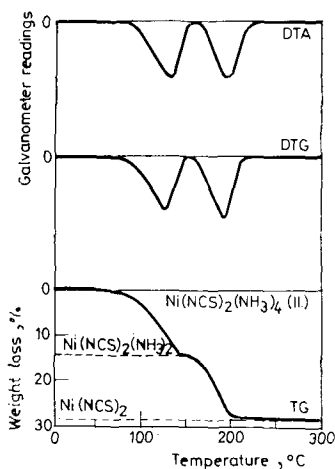
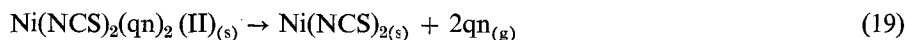
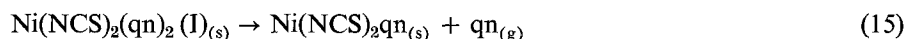


Fig. 3. Thermal curves of complex II

Since neither the number nor the position of bands in the electronic and infrared spectra, nor the powder diffractograms showed any differences, the reasons for the different stoichiometries of thermal decomposition for complexes I and II must be rather sought for in physical effects, especially in different degrees of crystal defectiveness of the two substances [18]. Complex I, prepared by crystallization from solution, exhibits more regularly grown crystals, offering greater resistance to the diffusion of ammonia, so that the formation of the intermediate $\text{Ni(NCS)}_2(\text{NH}_3)_3$ is favored. Complex II, prepared by heterogeneous reaction, apparently has less perfectly developed crystals with more defects and cracks, so that ammonia vapour diffuses more easily from the reaction zone and

$\text{Ni}(\text{NCS})_2(\text{NH}_3)_2$ is formed directly. The above conception is supported by the fact that if we increase the sample of complex II and compress it, the resistance to diffusion and also the ammonia concentration reaction interphase are both increased, and the thermoanalytical curves register the complex $\text{Ni}(\text{NCS})_2(\text{NH}_3)_3$, too.

To study the influence of the size of the particles on the stoichiometry of thermal decomposition, the complex $\text{Ni}(\text{NCS})_2(\text{qn})_4 \cdot 2\text{H}_2\text{O}$ (qn = quinoline) was taken as starting complex, since it can be prepared in coarse-crystalline form. Via indirect physical methods [19, 27] and also direct X-ray structure analysis [28], the starting compound was found to have the molecular structure $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{qn})_2] \cdot 2\text{qn}$, i.e. only half the quinoline molecules are coordinated. Further, it has been found [19] that the said complex exhibited different stoichiometries of thermal decomposition for the coarse-crystalline (cc.) form and the powder (p.) form. The processes can be expressed by Eqs (13–19):



After the release of water and the decomposition of the crystal structure, the thermal decomposition process yields a quinoline solution, from which the thermodynamically more stable isomer $\text{Ni}(\text{NCS})_2(\text{qn})_2$ (I) crystallizes, with a square planar configuration; this undergoes further decomposition in two steps [19].

In the decomposition of the starting compound in the powder form the liquid phase was not observed macroscopically (part of the quinoline being adsorbed on the solid reaction product). Due to this circumstance the pseudo-octahedral isomer $\text{Ni}(\text{NCS})_2(\text{qn})_2$ (II) was formed. This isomer shows a hexacoordinated tetragonal-bipyramidal structure, with the two NCS groups coordinated in different ways: as a terminal and a bridging group [17]. This isomer continues to decompose in one step.

The apparent and the real stoichiometries of thermal decomposition

The stoichiometry of thermal decomposition is often determined only by thermoanalytical methods (especially TG). The thermal analysis by itself is not always sufficient to determine the real stoichiometry of thermal decomposition. Until the

results of thermal analysis are not verified by phase analysis and by other methods, respectively, we may only speak of an apparent (instrumental) stoichiometry of thermal decomposition.

On the basis of the thermal decomposition of $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_4$ [20], we will show the possibility of different interpretations of the results by using the thermal analysis in itself and by combining it with the study of phase analysis (RTG) and spectral analysis (IR spectra). It follows from the TG and DTG curves of the complex under investigation (Fig. 4a – full line) that the apparent stoichiometry of thermal decomposition may be expressed by the scheme:

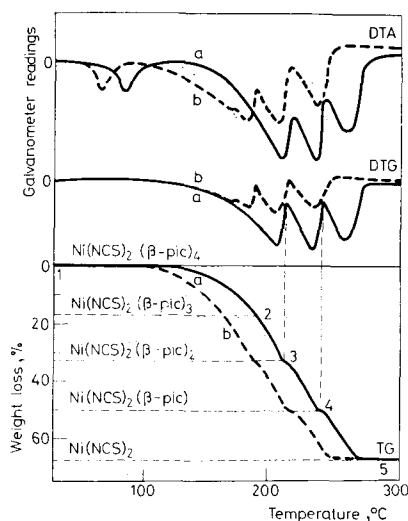
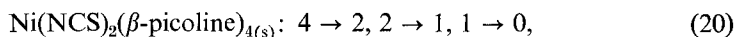


Fig. 4. Thermal curves of $\text{Ni}(\beta\text{-pic})_4(\text{NCS})_2$. The rate of temperature increase: a — $3^\circ/\text{min}$, b — $1.5^\circ/\text{min}$

i.e. the volatile ligands are released in three steps (the endothermic effect in the DTA curve before the loss of weight is due to a phase transformation). To verify the above stoichiometry, the starting compound and the thermal decomposition products were submitted to phase analysis at points 1 to 5, Fig. 4a (TG curve).

The results of diffraction analysis indicated the existence of even three intermediates and a four-step decomposition stoichiometry of $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_{4(s)}: 4 \rightarrow 3, 3 \rightarrow 2, 2 \rightarrow 1, 1 \rightarrow 0$.

The results of diffraction and thermal analyses are apparently in contradiction with each other, since on thermal analysis (rate of temperature increase $3^\circ/\text{min}$, sample weight 100 mg) the intermediate $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_3$ was not observed (curves a in Fig. 4). If, however, the same compound decomposed at a temperature increase rate of $1.5^\circ/\text{min}$, the DTG and DTA curves (curves b in Fig. 4)

showed a bend corresponding to the intermediate $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_3$.

The four-step reaction course of the thermal decomposition of the compound studied is also confirmed by spectral analysis (Table 3).

Table 3

Spectral data for the starting compound and the thermal decomposition products (in cm^{-1})

| Notation | Compound | $\tilde{\nu}(\text{C-N})$ |
|----------|--|---------------------------|
| 1 | $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_4$ | 2079 |
| 2 | $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_3$ | 2127, 2077 |
| 3 | $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_2$ | 2120 |
| 4 | $\text{Ni}(\text{NCS})_2(\beta\text{-picoline})_1$ | 2145, 2119 |
| 5 | $\text{Ni}(\text{NCS})_2$ | 2167 |

Since a change in the coordination of the NCS group must take place on the release of β -picoline with an unchanged coordination number of 6 [21], the $\tilde{\nu}(\text{C-N})$ vibrations in the infrared spectra were investigated. Owing to the successive release of the volatile ligand, the monodentate NCS group becomes bidentate or even tridentate. For intermediates with an odd number of β -picoline molecules, the functional character of the two NCS groups are expected to be different [20], while for compounds with an even number of β -picoline molecules as well as for $\text{Ni}(\text{NCS})_2$ the thiocyanate groups will be bonded in the same way. The expected type of coordination of the NCS groups was proved by spectral analysis (Table 3). Thermal analysis is apparently less sensitive than diffraction and spectral analysis.

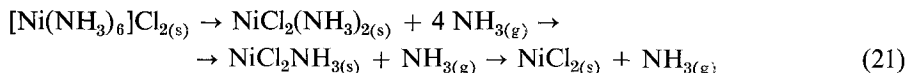
Analogous results were found in studying the stoichiometry of thermal decomposition for isothiocyanato-nickel(II) complexes with some alkylamines [6, 7].

The influence of ligand properties on the stoichiometry of thermal decomposition of nickel(II) coordination compounds

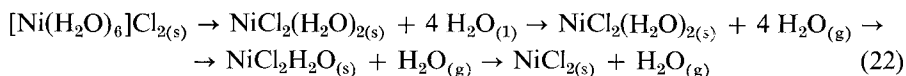
The stoichiometry of thermal decomposition of coordination compounds may also be influenced by the properties of the ligands. The stoichiometry of thermal decomposition depends on whether monodentate or polydentate ligands (chelates) are coordinated, and whether volatile ligands (released without themselves being decomposed) or non-volatile ligands (undergoing decomposition) or possibly a volatile molecule is present in the primary or secondary coordination sphere.

For complexes with non-volatile ligands of the chelate type (e.g. oximes) [2] their thermal decomposition does not usually occur by the splitting of metal-donor atom bonds, but by the splitting of some bond of the chelate ring, which means that the ligands themselves are decomposed and the interpretation of the results becomes rather difficult.

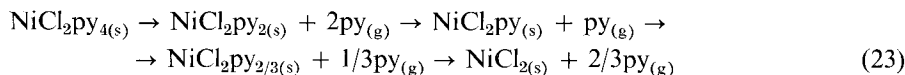
The influence of different types of neutral ligands follows from the study of the thermal decompositions of coordination compounds of the composition NiCl_2L_n , where $\text{L} = \text{NH}_3, \text{H}_2\text{O}, \text{py}$ or tu ($\text{tu} = \text{thiourea}$), and $n = 6$ or 4 . The thermal decomposition of the compound $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ takes place in three defined steps [22]:



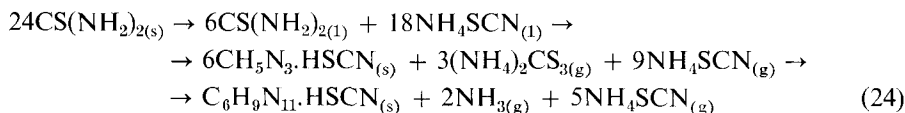
For $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ incongruent melting sets in [23]. This leads to a lower hydrate and a saturated solution, and may be expressed by the equations:



Though pyridine ($\text{L} = \text{py}$) and thiourea ($\text{L} = \text{tu}$) form compounds of the same composition $[\text{NiCl}_2\text{L}_4]$, they differ markedly in their stoichiometries of thermal decomposition. $[\text{NiCl}_2\text{py}_4]$ undergoes decomposition in four steps [24], involving the existence of the compound $\text{NiCl}_2\text{py}_{2/3}$:

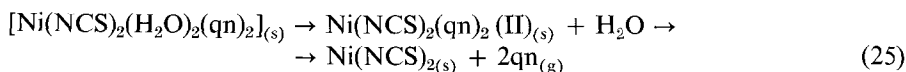


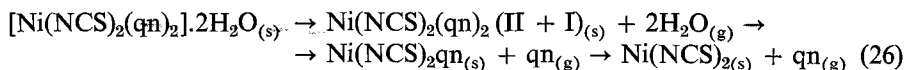
For the compound $[\text{NiCl}_2\text{tu}_4]$ the neutral ligand itself undergoes a complicated decomposition, which may be expressed by the following equations [25]:



i.e. in the first step a partial conversion of thiourea to ammonium thiocyanate takes place. Then guanidine thiocyanate is formed, which changes at 270° to melam thiocyanate. These decomposition products may react with the other complex components and consequently, the elucidation of the processes occurring becomes extremely difficult and it is hard to express them by simple equations [26].

The stoichiometry of thermal decomposition may also be influenced by the presence of a volatile molecule in the primary (ligand) or secondary coordination sphere. In this connection, the thermal decompositions of two hydrate isomers of the compositions $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{qn})_2]$ and $[\text{Ni}(\text{NCS})_2(\text{qn})_2]\cdot 2\text{H}_2\text{O}$ [29, 30] were studied, and especially the influence of the differently bonded water molecules on the stoichiometry of thermal decomposition. Significant differences were found [30] not only in the energies necessary for their removal and the change of the crystal structure, but also in the stoichiometry of thermal decomposition [30], as is to be seen from the equations:





Thermal decomposition of the hydrate isomer with coordinated water molecules yields an octahedral isomer of $\text{Ni}(\text{NCS})_2(\text{qn})_2$ (II) [30], see p. 220), which undergoes further decomposition in one step [21]. From the other hydrate isomer again an octahedral isomer of $\text{Ni}(\text{NCS})_2(\text{qn})_2$ (II) is formed, but with a small amount of square planar isomer (I). The nuclei of isomer (I) then catalyze its formation in the whole sample, and it appears in a two-step process in the further decomposition.

Stoichiometry of thermal decomposition and stereochemical changes of solid nickel(II) complexes

The multi-step stoichiometry of thermal decomposition of solid nickel(II) complexes has been explained in two ways [36]:

a) The volatile ligands in the starting complex are coordinated to Ni(II) with equal energies and are therefore equivalent. The differences between the originally equivalent ligands shown in the thermoanalytical curves may then be due to a stereochemical change after the escape of a certain amount of volatile ligand.

b) The volatile ligands are already not equivalent in the starting complex.

In elucidating the two-step thermal decomposition of the complex $\text{Ni}(\text{NCS})_2$ -(pyridine)₄, the author of paper [36] inclines to possibility b) (see page 215), the influence of stereochemical changes on the stoichiometry of thermal decomposition may in general not be excluded. For Ni(II) complexes various stereochemical changes are characteristic (square planar → octahedral, square planar → tetrahedral, octahedral → tetrahedral, etc. [21, 37, 38], as also the formation of configuration isomers [6, 17, 27, 31–33]).

Since stereochemical changes may influence the stoichiometry of thermal decomposition, the question arises as to the cases in which stereochemical changes can be expected in the thermal decomposition of nickel(II) complexes, and what causes them.

a) Study of factors affecting square planar → octahedral changes in thermal decomposition reactions (without isomer formation)

Stereochemical changes were studied in the thermal decomposition of complexes of the type $\text{Ni}(\text{NCS})_2\text{L}_2$ (L = mepy and me₂py). The investigated complexes undergo a one-step or two-step decomposition and for some of them square planar → octahedral changes take place [35]. The stereochemistries of the starting complexes and of their decomposition products are summarized in Table 4.

As Table 4 shows, complexes of type $\text{Ni}(\text{NCS})_2\text{L}_2$ with an alkyl substituent in position 2 (α -position) on the pyridine ring decompose in one step and a configurational change takes place:

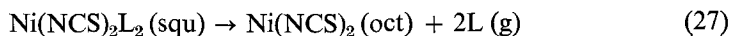


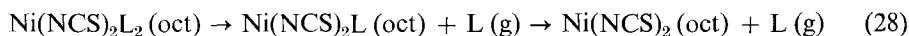
Table 4

Stereochemistry of complexes of the type $\text{Ni}(\text{NCS})_2\text{L}_n$ ($n = 2, 1, 0$)

| L | n | | |
|------------------------|-----|-----|-----|
| | 2 | 1 | 0 |
| 2-mepy | squ | — | oct |
| 2,4-me ₂ py | squ | — | oct |
| 2,5-me ₂ py | squ | — | oct |
| 2,6-me ₂ py | squ | — | oct |
| 3-mepy | oct | oct | oct |
| 4-mepy | oct | oct | oct |
| 4-etpy | oct | oct | oct |
| 3,4-me ₂ py | oct | oct | oct |

squ = square planar configuration, oct = octahedral configuration, mepy = methylpyridine, me₂py = dimethylpyridine

while complexes of the same composition, but for which the α -position with respect to the heterocyclic nitrogen atom is only occupied by hydrogen atoms, release volatile ligands L in two steps and no stereochemical change occurs:



Thus, the presence of the alkyl group in the α -position on the pyridine ring significantly influences the steric and electronic properties of the ligands and thereby also the stereochemical changes of the respective nickel(II) coordination compounds in the thermal decomposition. The position of the alkyl substituent on the pyridine ring also influences the stoichiometry of thermal decomposition (Table 4). The fact found that square planar complexes of the type $\text{Ni}(\text{NCS})_2\text{L}_2$ (substituent in the α -position), decompose in one step, while octahedral compounds exhibit two steps, does not apply generally, however [21] (e.g. the square planar complex $\text{Ni}(\text{NCS})_2(\text{qn})_2$ decomposes in two steps). The stoichiometry of thermal decomposition is affected by still other factors (page 217 and others).

b) Study of factors influencing the formation of configuration isomers in thermal decomposition reactions

The study of the stoichiometry of thermal decomposition becomes complicated if configuration isomers are formed, or if their mutual changes take place due to temperature influence.

From the point of view of the formation of configuration isomers, the thermal decomposition of compounds of the type $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2\text{L}_2] \cdot 2\text{L}$, where L = qn [19], 4-meqn [31], and 6-meqn [33] (me = methyl, qn = quinoline) is interesting, since they have a pseudo-octahedral configuration. After the release of water and 2L, heating yields compounds of the composition $\text{Ni}(\text{NCS})_2\text{L}_2$, which can have octahedral or square planar configurations (I, II, or possibly I and II), as is to be seen in Fig. 5.

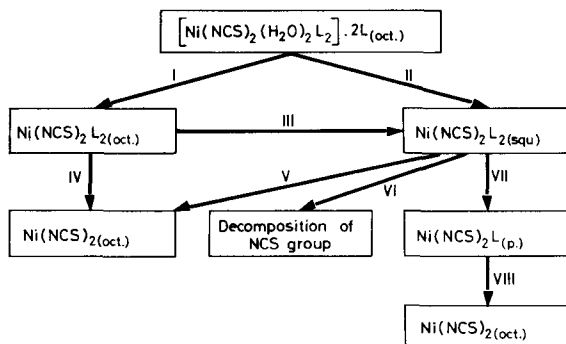


Fig. 5. Thermal decomposition of compounds of the type $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2\text{L}_2] \cdot 2\text{L}$, where $\text{L} = \text{qn}$, 4-meqn and 6-meqn; oct = octahedral, squ = square planar, p = pentacoordinated complex

The thermal decompositions of the starting compounds (for different L) do not proceed equally. For 4-meqn the reaction occurs via II and VI, for 6-meqn via II and V, and for qn the possibility of formation of both isomers of the composition $\text{Ni}(\text{NCS})_2\text{L}_2$ is given. Depending on the experimental conditions (page 217), after the release of water and of 2/4 quinoline either the molecules of $\text{Ni}(\text{NCS})_2\text{qn}_2$ with square planar configuration are formed (which undergo further decomposition in two steps: $\text{II} \rightarrow \text{VII} \rightarrow \text{VIII}$), or the fifth and sixth positions in the coordination octahedron are occupied by new donor atoms to form the pseudo-octahedral isomer $\text{Ni}(\text{NCS})_2\text{qn}_2$ (decomposed in one step: $\text{I} \rightarrow \text{IV}$) [17, 19]. The conversion of the octahedral isomer to the square planar isomer (III) takes place for all compounds of the type $\text{Ni}(\text{NCS})_2\text{L}_2$ (for $\text{L} = \text{qn}$, however, only in the presence of liquid quinoline).

Since the configuration isomers influence the stoichiometry of thermal decomposition (they decompose differently), the factors were investigated which affect their formation in the solid state.

In the thermal decomposition of the starting coordination compounds the possibility of the formation of both isomers exists, depending on the suitable electronic and steric properties of the ligands [3].

The fact that both isomers arise on thermal decomposition only for $\text{L} = \text{qn}$, is due to the small difference in the decomposition enthalpies for isomers with quinoline [34], while for those with 4-meqn and 6-meqn the square planar isomer is more stable. The preparation of this isomer by the thermal decomposition reaction of a solid starting compound depends on different experimental conditions (size of the particles, page 220, Eqs 13–19).

In the isomerization reactions, the thermal decomposition reactions of the hydrate isomers of the composition $\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{qn})_2$ may also be included (page 223, Eqs 25, 26).

Conclusions

The study was concerned with factors influencing the stoichiometry of thermal decomposition of solid nickel(II) coordination compounds. We found three basic factors:

1. *Crystal structure*: this influences the stability of the complex species in the solid phase and may affect the stoichiometry of thermal decomposition from two aspects:

a) from the thermodynamic aspect: certain intermediates are thermodynamically unstable and therefore less intermediates are formed;

b) from the kinetic aspect: certain intermediates arise slowly so that again less intermediates can be identified.

In the search for correlations between structural factors and the stoichiometry of thermal decomposition, every reaction steps must be analyzed separately (i.e. it is necessary to know the crystal structures of all intermediates). It is not possible to predict the stoichiometry of thermal decomposition (the number of defined intermediates) only from the structural data of the starting complex.

2. *Experimental conditions*: these influence not only the courses of the thermo-analytical curves and the decomposition temperatures, but also the stoichiometry of thermal decomposition. They include not only methodical and instrumental effects, but also the mode of preparing the compounds investigated, size of the particles, etc.

3. *Ligand properties*: the stoichiometry of thermal decomposition also depends on whether there are volatile ligands, or ligands undergoing decomposition, monodentate or polydentate ligands (chelates), or volatile molecules in the primary (ligand) or in the secondary coordinating sphere, on the positions and the natures of substituents on a volatile ligand (especially the position with respect to the donor atom), etc.

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RÉSUMÉ — L'article considère les facteurs chimiques et physiques qui influencent la stœchiométrie des réactions de décomposition thermique des composés de coordination solides. Les composés de coordination du nickel(II) ont été choisis pour illustrer le problème des relations entre la structure du composé initial (et de ses intermédiaires) et la stœchiométrie de la réaction de décomposition thermique. On montre que les conditions expérimentales influencent la décomposition et on discute le principe des réactions stœchiométriques de décomposition thermique dites « apparentes » et « réelles ». Les résultats obtenus sont probablement de portée plus générale.

ZUSAMMENFASSUNG — Der Beitrag befaßt sich mit den chemischen und physikalischen Faktoren, welche die Stöchiometrie der thermischen Zersetzung fester Koordinationsverbindungen beeinflussen. Koordinationsverbindungen von Nickel(II) wurden als Beispiel eingesetzt; das Problem des Zusammenhanges zwischen Struktur der Ausgangsverbindung (und seiner Intermediärprodukte) und der Stöchiometrie der thermischen Zersetzung wird erörtert; die die Zersetzung beeinflussenden Versuchsbedingungen werden gezeigt und das Konzept der sogenannten scheinbaren und tatsächlichen Stöchiometrie der thermischen Zersetzung wird beschrieben. Die erhaltenen Ergebnisse dürften von allgemeinerer Bedeutung sein.

Резюме — В статье рассматриваются химические и физические факторы, затрагивающие стехиометрию термического разложения твердых координационных соединений. На примере координационных соединений никеля(II) была обсуждена взаимосвязь между структурой начального соединения (и его промежуточных продуктов) и стехиометрией термического разложения. Показаны экспериментальные условия, затрагивающие это разложение, и обсуждена концепция так называемой кажущейся и истинной стехиометрии термического разложения. Полученные результаты могут иметь более общее значение.