Heterogeneous reactions of solid nickel(II) complexes. X. Study of stoichiometry of thermal decomposition of isothiocyanatonickel(II) complexes with some alkylamines

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The stoichiometry of thermal decomposition of isothiocyanatonickel(II) complexes with some alkylamines was studied by means of thermoanalytical methods. It has been found that the complex $Ni(NCS)_2(methylamine)_4$ (*I*) decomposes in three steps (−2, −1, −1), $Ni(NCS)_2(ethylamine)_4$ (*II*) in two steps (−2, −2), and both isomeric forms (pseudooctahedral and square-planar) of the complex $Ni(NCS)_2(diethylamine)_2$ (*VI*) and (*V*) in one step (−2). For complex *I* the diffraction and spectral analyses (the i.r.) also evidenced the existence of the intermediate $Ni(NCS)_2(methylamine)_3$. It was stated that the more-step release of volatile ligands for complexes *I* and *II* is not connected with a stereochemical change in the course of the thermal decomposition (no change of the shape of the coordination polyhedron occurs), but rather with fine differences in their crystal structure (*e.g.* mutual interactions of structure units in the crystal).

При помощи термоаналитических методов изучалась стехиометрия термического разложения изотиоцианато комплексов двухвалентного никеля с некоторыми алкиламинами. Было найдено, что комплекс $Ni(NCS)_2$(метиламин)$_4$ (*I*) разлагается в три стадии (−2, −1, −1), комплекс $Ni(NCS)_2$(этиламин)$_4$ (*II*) разлагается в две стадии (−2, −2), а два изомера псевдооктаэдрический и квадратный комплекса $Ni(NCS)_2$(диэтиламин)$_2$ (*VI* и *V*) разлагаются в одной стадии (−2). Для комплекса *I* рентгенофазовый анализ и инфракрасные спектры поглощения подтвердили также существование промежуточного продукта $Ni(NCS)_2$(метиламин)$_3$. Было показано, что многоступенчатое выделение летучих лигандов из комплексов *I* и *II* не зависит от стереохимического изменения во время термического разложения (не ведет к изменению координационного полиэдра), и вероятно связано с тонкими различиями в их кристаллической структуре (например, взаимные интеракции структурных единиц в кристалле).

In our former works we were occupied with the study of factors influencing the stoichiometry of thermal decomposition of solid nickel(II) complexes [1—5]. It has been found that also in studying the decomposition stoichiometry great attention must be paid to instrumental and methodical factors (as *e.g.* the heating rate [1, 2], the influence of the

pressure and composition of the gaseous phase [2]), as well as to the physical and chemical properties of the complexes under investigation (as grain size [3], crystal deffectivity caused by different preparation [4], different composition of the primary coordination sphere [5], isomerization processes [3, 5]).

This work deals with the study of the thermal decomposition stoichiometry of complexes of the type $Ni(NCS)_2B_n$ ($n = 4$, B = methyl-, ethylamine, and $n = 2$, B = diethylamine, respectively, red and green isomers [6, 7]), the experimental conditions having been kept constant. This study represents a part of a more extensively based problem complex, the aim of which is to gain new knowledge of the mechanism of thermal decomposition reactions for nickel(II) complexes in the solid state.

Experimental

The chemicals used, analytical methods, preparation and the analysis results for the complexes $Ni(NCS)_2B_4$ (B = methylamine = ma, ethylamine — ea) are given in [6]. In addition to heterogeneous reactions these complexes may be also prepared from solutions, analogically as complex $Ni(NCS)_2(NH_3)_4$ [4]. The method of their preparation has, however, no influence on the stoichiometry of their thermal decomposition.

This paper further presents the results obtained from crystalline samples prepared from solution. The preparation and the analysis results of the couple of isomers of $Ni(NCS)_2$(diethylamine)$_2$ (diethylamine = dea) are given in [6, 7].

The thermal analysis was studied with a derivatograph (MOM, Budapest) of the type OD 102, in an air atmosphere and at a heating rate of 3°C/min. Platinum crucibles were used with an upper diameter of 14 mm, the weighing sample was 100 mg. The decomposition products of the investigated complexes were prepared analogically as in [8].

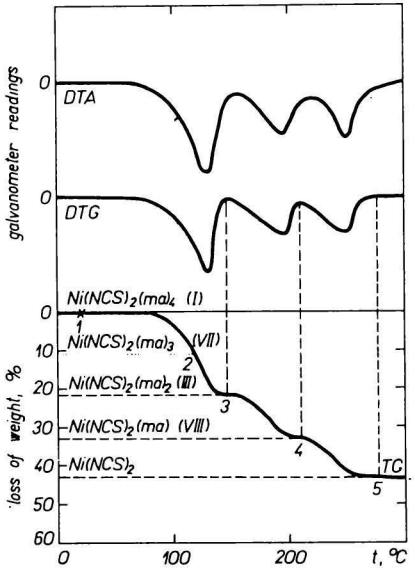

Fig. 1. DTA, DTG, and TG curves of the complex $Ni(NCS)_2(ma)_4$ (*I*).

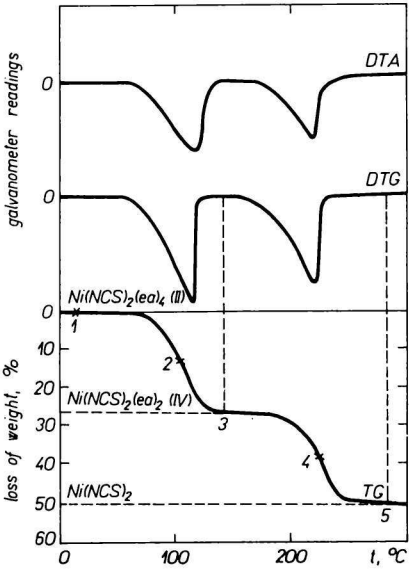

Fig. 2. DTA, DTG, and TG curves of the complex $Ni(NCS)_2(ea)_4$ (*II*).

The electronic absorption spectra were measured using a Specord UV VIS (Zeiss, Jena) spectrophotometer in the region 12—30 000 cm^{-1}. The infrared absorption spectsra of the solid samples in KBr were measured in the region 400—4000 cm^{-1} with a double-beam UR-10 (Zeiss, Jena) spectrophotometer. The spectra in the region 200—450 cm^{-1} were measured with a Perkin—Elmer apparatus 225.

Results and discussion

In the thermal decomposition of complexes of the type $Ni(NCS)_2B_4$ (B = volatile nitrogen ligand), in principle the volatile ligands may be released in one step, *i.e.* all the four ligands B at the same time. More often, however, it is a more-step process, when one or two ligands B successively escape, according to the equations [8]

$$Ni(NCS)_2B_4(s) \rightarrow Ni(NCS)_2B_3(s) + B(g), \quad (1)$$

$$Ni(NCS)_2B_3(s) \rightarrow Ni(NCS)_2B_2(s) + B(g), \quad (2)$$

$$Ni(NCS)_2B_2(s) \rightarrow Ni(NCS)_2B(s) + B(g), \quad (3)$$

$$Ni(NCS)_2B(s) \rightarrow Ni(NCS)_2(s) + B(g), \quad (4)$$

$$Ni(NCS)_2B_4(s) \rightarrow Ni(NCS)_2B_2(s) + 2B(g), \quad (5)$$

$$Ni(NCS)_2B_2(s) \rightarrow Ni(NCS)_2(s) + 2B(g). \quad (6)$$

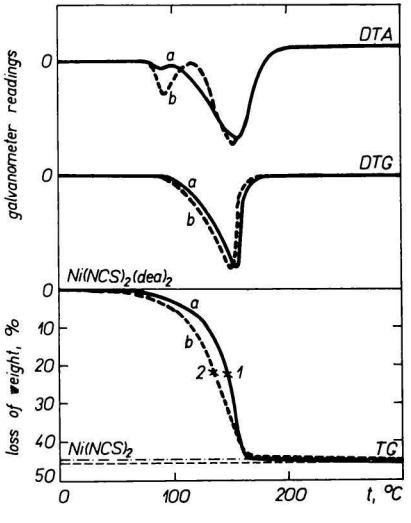

Fig. 3. DTA, DTG, and TG curves of two isomers of the complex $Ni(NCS)_2(dea)_2$: *a*) complex *V*; *b*) complex *VI*.

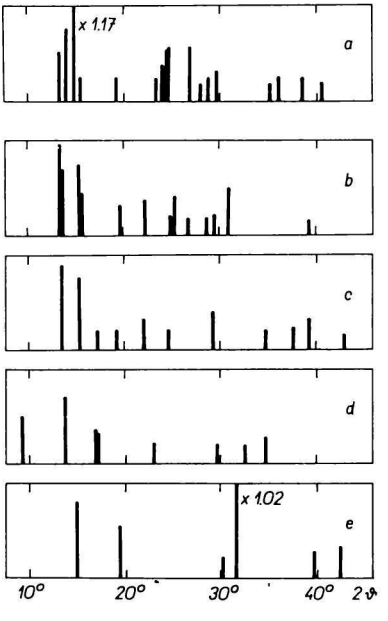

Fig. 4. Powder-diffractograms. *a*) Complex *I*; *b*) complex *VII*; *c*) complex *III*; *d*) complex *VIII*; *e*) $Ni(NCS)_2$.

In dependence on the type of the ligand B some of the presented steps have not been observed. To determine the different reaction steps (the so-called instrumental stoichiometry of thermal decomposition) thermoanalytical methods were applied. The DTA, DTG, and TG curves of the investigated complexes with alkylamines are shown in Figs. 1—3.

From the derivatogram of the complex $Ni(NCS)_2(ma)_4$ (*I*) (Fig. 1) and $Ni(NCS)_2(ea)_4$ (*II*) (Fig. 2) the following conclusions may be drawn: Complex *I* is of stable weight up to 70°C, while complex *II* to 65°C. The thermal decomposition of complex *I* takes place in three steps while that of complex *II* in two steps. The losses of weight corresponding to the different decomposition steps for complex *I* (21.0, 31.0, and 43.0%) and for complex *II* (25.0 and 51.0%) are in a good agreement with the calculated values (−2 ma: 20.77%, −3 ma: 31.15%, −4 ma: 41.53%, and −2 ea: 25.37%, −4 ea: 50.76%, respectively). The maxima of the decomposition rate of the different processes are at 125, 195, and 250°C for complex *I*, and at 115 and 220°C for complex *II*. As the DTA curves show, in the decomposition of both complexes only endothermic processes take place. The instrumental stoichiometry of the thermal decomposition of complex *I* may then be expressed by eqns (*5*), (*3*), and (*4*), *i.e.* the following intermediates were identified on the thermoanalytical curves: $Ni(NCS)_2(ma)_2$ (*III*) and $Ni(NCS)_2(ma)$ (*VIII*). The decomposition stoichiometry of complex *II* corresponds to the eqns (*5*) and (*6*) and the intermediate $Ni(NCS)_2(ea)_2$ (*IV*) was found.

The derivatograms of the square (*V*) and the pseudooctahedral (*VI*) isomers of the complex $Ni(NCS)_2(dea)_2$ (Fig. 3) show that the isomer *V* is of stable weight up to 60°C, isomer *VI* up to 45°C. Both isomers decompose in one step. The respective losses of weight for isomer *V* (45.0%) and isomer *VI* (44.5%) are in a good agreement with the calculated value (45.53%). These steps may be identified also by means of the DTG curves. The maxima of the decomposition rate are at 155°C (isomer *V*) and 150°C (isomer *VI*). The instrumental stoichiometry of decomposition for both the isomers may then be expressed by eqn (*6*).

In addition to the main deviations at 155°C (isomer *V*) and 150°C (isomer *VI*), respectively, corresponding to the escape of two moles diethylamine, the DTA curves show for both isomers also a less intensive deviation at 90°C. This deviation does not indicate a mutual conversion of the isomers, but the formation of the liquid phase, as it was seen from the diffractograms and also by macroscopic observation. The powder diffractograms of the products *1* and *2* (see the TG curves in Fig. 3) further indicate that on the escape of 20% diethylamine, the intensity of the diffraction lines expressively decreases, *i.e.* an amorphous intermediate is being formed which on interruption of the decomposition is wet from the released diethylamine. The final decomposition product up to 300°C is for both isomers the already crystalline $Ni(NCS)_2$. Thus the decomposition process is more complicated than eqn (*6*) indicates.

Complexes *I* and *II* of the composition $Ni(NCS)_2B_4$ release volatile ligands in several steps. The authors [9, 10] explain this circumstance with the change of stereochemistry during the thermal decomposition, causing a difference between the originally equivalent molecules B, or with the suggestion that due to influences on the ligands in the crystal structure, the four ligands B are already in the starting complex not equivalent. To elucidate these questions the stereochemical properties of the complexes under investigation were studied by means of electronic absorption spectra and the character of the bonds Ni—N (ammine) was studied by means of the i.r. spectra.

Complexes *I* and *II* exhibit [6] a pseudooctahedral structure with end-bonded NCS groups, complexes *III* and *IV* prepared by interruption of the thermal decomposition [8] (likewise as those obtained by isothermal heating) have also a pseudooctahedral con-

figuration, however, with bifunctional bonded NCS groups [6]. Also complex *VII* is characterized by the coordination number 6, this case demands, however, differently bonded (bifunctional and trifunctional) NCS groups, as it also follows from spectral measurements ($\tilde{\nu} = 15\,750$ and 27 600 cm^{-1}, and $\tilde{\nu}$(C—N) = 2129 and 2151 cm^{-1}, respectively). The final product up to 300°C is $Ni(NCS)_2$ having a pseudooctahedral structure with trifunctional NCS groups [11]. The stereochemical properties of complexes *I* and *II* and of their decomposition products may be expressed by eqn (*7*)

$$Ni(NCS)_2B_4(oct) \rightarrow Ni(NCS)_2B_2(oct) \rightarrow$$
$$\rightarrow Ni(NCS)_2B\ (only\ ma)(oct) \rightarrow Ni(NCS)_2(oct)$$

i.e. during the thermal decomposition the shape of the coordination polyhedron did not change.

The data of the infrared absorption spectra are shown in Table 1. In the region of N—H vibrations complex *I* (differently from complexes *II* and *IV*) shows 4 bands instead of the expected two ones. This may be due to the unequivalent bonding of the methylamine molecules or to mutual interaction of structure units in the crystal [12]; the presence of uncoordinated methylamine molecules is, however, according to the electronic spectrum of complex *I*, excluded [6]. The absorption bands corresponding to the Ni—N (ammine) vibration are for ammine complexes of Ni(II) in the region 330—400 cm^{-1} [4, 13]. For complexes with alkylamines is expected, due to the induction effect of the alkyl group, the Ni—N (ammine) bonding to become stronger thus causing the decrease of the strength of the N—H bonding (proved also experimentally; Table 1). The bands of the Ni—N (ammine) stretching vibration did, however, not confirm non-equivalently bonded ligands. Little sensibility of this vibration for similar purposes was also found by the authors [8—10].

Based on the found differences in N—H vibrations for complexes *I* and *II* also a different number of steps of their thermal decomposition might be expected. The intermediates *III* and *VIII* for complex *I* and the intermediate *IV* for complex *II* were directly recorded on

Table 1

Values of the wavenumbers (in cm^{-1}) of the complexes *I*—*IV* (for comparison purposes also of complex $Ni(NCS)_2(NH_3)_4$) and of the decomposition products of the complex *I*

Complex	$\tilde{\nu}_{as}(NH_2)$	$\tilde{\nu}_{s}(NH_2)$	$\tilde{\nu}$(Ni—N) ammine	Complex	$\tilde{\nu}$(C—N)
$Ni(NCS)_2(NH_3)_4$	3360	3270	330	*I*	2108
I	3320	3271	345	*VII*	2106
	3300	3252		(-1 ma)	2125
II	3304	3250	415	*III*	2135
				(-2 ma)	
III	3312	3265	382	*VIII*	2129
				(-3 ma)	2151
IV	3314	3263	410	$Ni(NCS)_2$	2167

the thermoanalytical curves (Figs. 1 and 2). That does, however, not yet prove that complexes $Ni(NCS)_2B_3$ (B = ma, and ea, respectively) do not exist, especially when complex $Ni(NCS)_2(NH_3)_3$ is known [4] and its structure was studied by X-ray analysis [14]. Further, for the complex $Ni(NCS)_2$(3-methylpyridine)$_4$ (sample weight 100 mg) the thermoanalytical curves exhibited two intermediates (-2, -1), the phase and the spectral analyses proved, however, also the formation of $Ni(NCS)_2$(3-methylpyridine)$_3$ [1] which on the thermoanalytical curves was observed only for samples of higher weight (400 mg) and a thicker layer. Starting from the above said also complexes *I* and *II* were submitted to phase and spectral (the i.r.) analyses as well as the products of their thermal decomposition in points *1* to *5* on the TG curve in Fig. 1 (complex *I*) and in points *1* to *5* on the TG curve in Fig. 2 (complex *II*). The results of the diffraction analysis are shown in Fig. 4 and they prove three intermediates of the thermal decomposition of complex *I*: $Ni(NCS)_2(ma)_3$ (*VII*), $Ni(NCS)_2(ma)_2$ (*III*), and $Ni(NCS)_2(ma)$ (*VIII*). This finding is also supported by the results of spectral measurements (Table 1). Since on the release of one volatile ligand and for unchanged coordination number 6, a change of the coordination of the NCS group must take place, we investigated the respective $\tilde{\nu}$(C—N) vibrations. For the intermediates *VII* and *VIII* the functional character of the two NCS groups (in the same complex) is expected to be different, while for complexes *I*, *III*, and $Ni(NCS)_2$ both groups will be bonded equally. The expected mode of coordination of the NCS group for the thermal decomposition products of complex *I* was confirmed by the spectral analysis. (The couple of bands found for complexes *VII* and *VIII* numerically differ from the single bands corresponding to complexes *I* and *III*.) For complex *II* the diffraction analysis did not prove the existence of intermediates (-1 ea, -3 ea), though the diffractogram of the product $\sim Ni(NCS)_2(ea)_3$ cannot be explained only by the simultaneous occurrence of the bands of complexes *II* and *IV*

In general the stoichiometry of thermal decomposition is influenced besides instrumental and methodical factors [2] also by the physical and chemical properties of the starting complexes [3—5], as well as by those of their decomposition products. The present work was devoted to the study of the relationship between the decomposition stoichiometry and the stereochemical factors of the starting complexes, and the finer structure changes, during their decomposition, respectively. Only a few papers in this field are known in the literature [9, 10, 12] and no unambiguous conclusions have been drawn. We have found a different decomposition stoichiometry for complexes *I* and *II* (under constant experimental conditions), the Ni—N (amine) vibrations did not record yet in the infrared spectra unequivalently bonded molecules of amines. For complex *I* (differently from complex *II*) we have observed, however, splitting of the bands corresponding to the N—H vibrations. The structure differences must therefore be very fine and they reach rather the region of the secondary coordination sphere (as the mutual interactions of structure units in the crystal are). A more detailed solving of this problem requests knowledge of the whole crystal structure of the starting complexes (the primary and the secondary coordination sphere). Such starting complexes will be the subject of our further study.

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