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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, III

THERMAL DECOMPOSITION OF COMPOUNDS OF THE TYPE $Ni(NCS)_2L_2$

PART A: THE STOICHIOMETRY OF DECOMPOSITION

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The thermal decompositions of solid complexes of the type $Ni(NCS)_2L_2$ (L = pyridine, α-picoline, β-picoline, 2,6-lutidine, and quinoline) were studied by means of the derivatograph. It was found that the decompositions of complexes with pyridine, α-picoline, 2,6-lutidine, and quinoline (the pseudo-octahedral complex) are one-step processes, and those of complexes with β-picoline and quinoline (the square-planar complex) consist of two steps.

Diffuse reflectance spectra were recorded to elucidate the structures of the decomposition intermediates.

The reasons for the different stoichiometries of decomposition for complexes of the same type are discussed.

In research into the reactivities of coordination compounds considerable attention is paid to the study of reactions of different isomeric compounds and their interconversions due to substitution processes. So far, however, mainly solution reactions have been studied, these being sufficiently slow to be approached by classical experimental methods [1, 2]. Since nickel(II) complexes in solution are not generally substitutionally inert, we tried to obtain data for isomeric compounds of Ni(II) in the solid state and so to contribute to the elucidation of the mechanisms of substitution reactions of solid nickel(II) complexes [3, 4].

Our work was directed to the study of the relationship between the structures of the two configurational isomers of $Ni(NCS)_2Q_2$ [5, 6] and their thermal decompositions (the stoichiometry of decomposition, thermochemical and kinetic data). In studying these relationships we attempted to draw conclusions for complexes of the same type and structure. Thus, other isothiocyanate nickel(II) complexes of the type $Ni(NCS)_2L_2$ (L = heterocyclic nitrogen base) of square-planar configuration (L = α-picoline and 2,6-lutidine) [7] and of pseudo-octahedral configuration (L = pyridine and β-picoline) [8, 9] were submitted to analogous study.

Experimental

The chemicals, analytical methods, preparation, and analytical results for both isomers have been reported in previous papers [5, 6]. The complexes $Ni(NCS)_2py_2$ (py = pyridine) and $Ni(NCS)_2(\beta\text{-pic})_2$ (β-pic = β-picoline) were prepared by thermal decomposition of the corresponding compounds of the type $Ni(NCS)_2L_4$, prepared analogously to $Ni(NCS)_2Q_4 \cdot 2H_2O$ (Q = quinoline) [5, 6]. The preparation of $Ni(NCS)_2 \cdot (\alpha\text{-pic})_2$ (α-pic = α-picoline) is presented in paper [10]. The red complex $Ni(NCS)_2(2,6\text{-lut})_2$ (2,6-lut = 2,6-lutidine) was prepared analogously. The results of the analysis are given in Table 1.

Table 1

Compound	Molecular weight	% Ni		% N	
		calcd.	found	calcd.	
$Ni(NCS)_2py_2$	333.06	17.62	17.55	16.82	16.91
$Ni(NCS)_2(\alpha\text{-pic})_2$	361.15	16.25	16.18	15.51	15.60
$Ni(NCS)_2(\beta\text{-pic})_2$	361.15	16.25	16.30	15.51	15.45
$Ni(NCS)_2(2,6\text{-lut})_2$	389.20	15.08	14.92	14.39	14.51

The thermal decompositions were studied by means of a derivatograph (MOM, Budapest). The apparatus and its operation are explained in paper [11]. Platinum crucibles with an upper diameter of 14 mm were used, and the thermocouples were Pt, Pt-Rh.

All the powder samples, with a grain size smaller than 0.06 mm, had a weight of 100 mg. The rate of temperature increase was 3°/min; the measurements were made in a nitrogen atmosphere, the rate of the nitrogen flow being 150 ml/min.

The powder diffractograms of the samples under investigation were taken with a GON III diffractograph (Chirana) which automatically recorded the diffracted radiation. The radiation used was CuKα. The scanning conditions are given in paper [4].

The diffuse reflectance spectra of the powder samples in the visible region were measured with an SF-10 spectrophotometer (U.S.S.R.). The solid samples were mixed with magnesium carbonate.

Results and discussion

I. The thermal decomposition of complexes with volatile nitrogen ligands (pyridine and its derivatives) has been intensively studied by many authors [12]. Only a few data are available on the thermal decomposition of isomeric coordination compounds. This is due to the thermal lability of one of the isomers, which is transformed on heating to a more stable form [13, 14]. This is the reason why authors often investigate the thermal decomposition only of the more stable isomer, in the case of the isomers of NiX_2Q_2, where Q = quinoline and X = Cl, Br [15]. So far, however, there are no reports of the thermal decomposition of $Ni(NCS)_2Q_2$, although these complexes were first prepared some time ago [16].

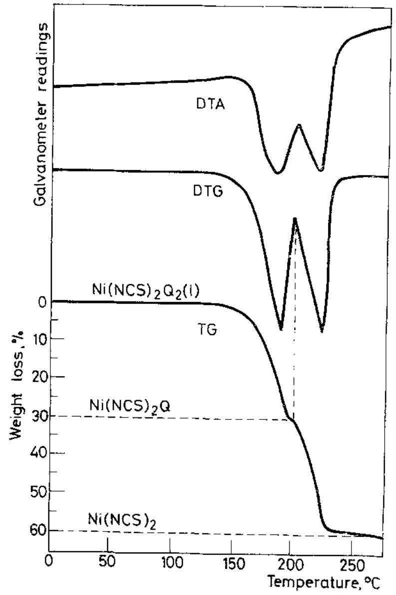

Fig. 1. Thermal curves of $Ni(NCS)_2Q_2$ *(I)*

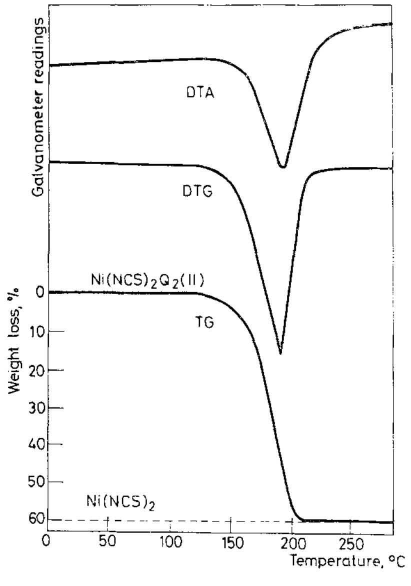

Fig. 2. Thermal curves of $Ni(NCS)_2Q_2$ *(II)*

The reasons are probably connected with the difficulties of their preparation [5, 6].

The derivatograms of isomer *I* (square-planar) (Fig. 1) and isomer *II* (tetragonal-bipyramidal) (Fig. 2) lead to the following conclusions: Isomer *I* shows constant weight up to 132°, while for isomer *II* this limit is 117°. The thermal decomposition of isomer *I* consists of two separate steps, while that of isomer *II* proceeds in one step. The losses of weight due to the different decomposition steps for isomer *I* (30.0 and 60.15 %, respectively) and for isomer *II* (59.5 %) show good agreement with the calculated values. The different steps may be clearly determined by means of the DTG curves; the maxima of the decomposition rates are at 189° and 224°, respectively, for isomer *I*, and at 187° for isomer *II*. According to the DTA curves, both isomers decompose endothermically. Under the given conditions, no conversion of isomer *II* to the thermodynamically more stable isomer *I* [16] was observed.

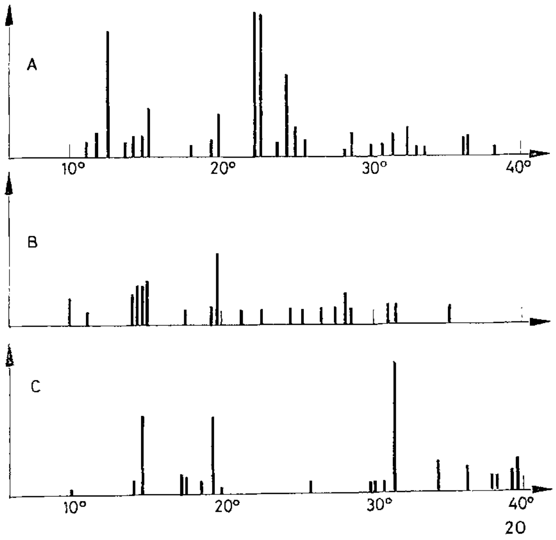

Fig. 3. Powder diffractograms: A — $Ni(NCS)_2Q_2$ *(I)*, B — $Ni(NCS)_2Q$, C — $Ni(NCS)_2$

The existence of the intermediate $Ni(NCS)_2Q$, resulting from decomposition of isomer *I*, was also proved by means of powder diffractograms (Fig. 3). The final product of decomposition of both isomers is $Ni(NCS)_2$, which contains a tetragonal coordination sphere with tridentate bridging NCS groups [17]. Hence, no change of coordination number occurs in the thermal decomposition of isomer *II*. In the case of isomer *I*, the intermediate $Ni(NCS)_2Q$ is formed; for this not only a coordination number of 6 may be considered (pseudo-octahedral configuration), but also one of 5 (trigonal-bipyramidal or tetragonal-pyramidal con-

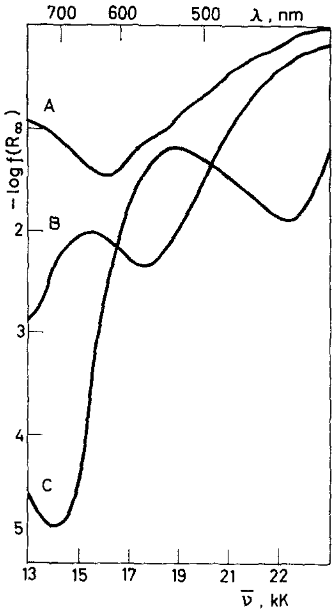

Fig. 4. Diffusion reflectance spectra: A — $Ni(NCS)_2Q$, B — $Ni(NCS)_2(\beta\text{-pic})$, C — $Ni(NCS)_2(2,6\text{-lut})_2$

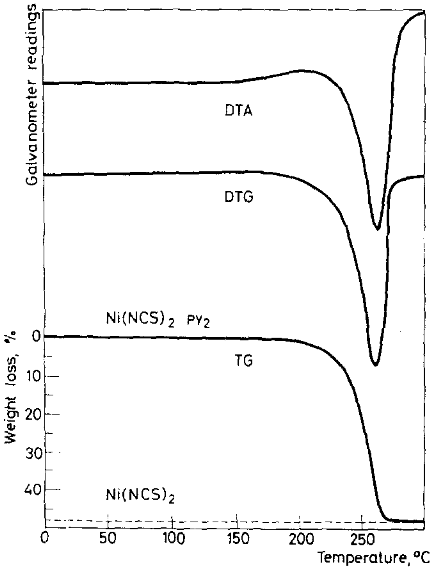

Fig. 5. Thermal curves of $Ni(NCS)_2py_2$

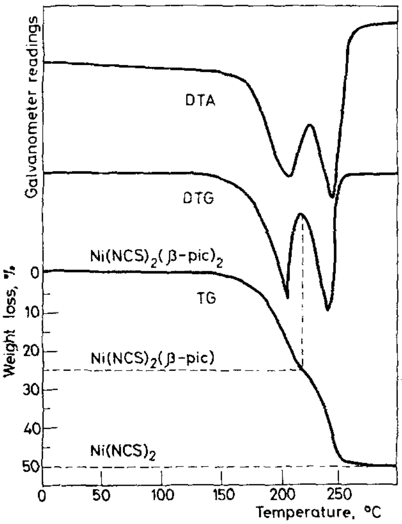

Fig. 6. Thermal curves of $Ni(NCS)_2(\beta\text{-pic})_2$

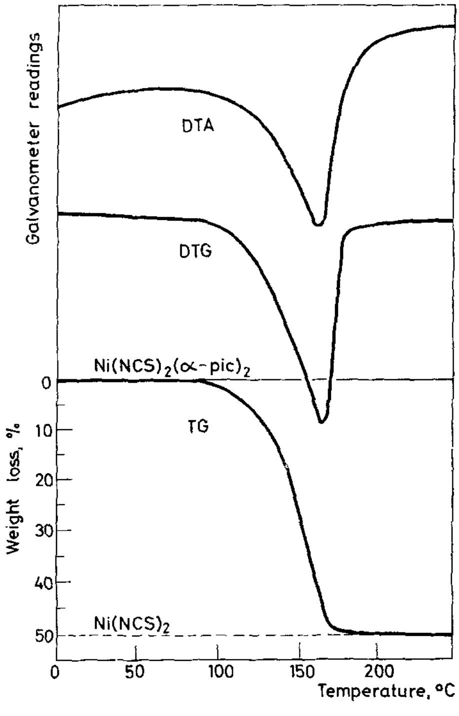

Fig. 7. Thermal curves of $Ni(NCS)_2(\alpha\text{-pic})_2$

figuration), or even of 4 (square-planar, or tetrahedral configuration). The diffuse reflectance spectra of $Ni(NCS)_2Q$ (Fig. 4, A) and literature data [8, 18, 19] show that only the trigonal bipyramidal or the tetragonal pyramidal arrangement can be considered, i.e. a coordination number of 5. This conclusion is supported by the analogous shapes of the absorption curves for $Ni(NCS)_2Q$ and for complexes of the type NiX_2L, where X = Cl, Br, NCS, and L is bis(2-dimethylaminoethyl)-oxide, for which a trigonal-bipyramidal structure is assumed, with the triplet ground state $^3E'(F)$ of D_{3h} symmetry [20].

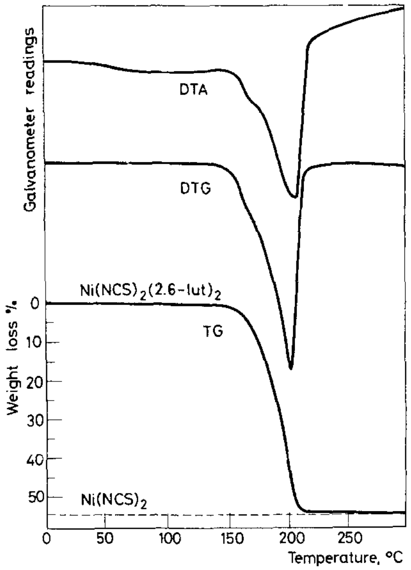

Fig. 8. Thermal curves of $Ni(NCS)_2(2,6\text{-lut})_2$

The coordination number of the complexes formed in the thermal decomposition of isomer *I* gradually increases. This may be expressed by the scheme:

$$Ni(NCS)_2Q_2\,(I)_{(\text{Coord. No. 4})} \rightarrow Ni(NCS)_2Q_{(\text{Coord. No. 5})} \rightarrow Ni(NCS)_{2(\text{Coord. No. 6})} \qquad (1)$$

II. Thermoanalytical curves of the mixed complexes $Ni(NCS)_2py_2$, $Ni(NCS)_2(\beta\text{-pic})_2$, $Ni(NCS)_2(\alpha\text{-pic})_2$ and $Ni(NCS)_2(2,6\text{-lut})_2$ are shown in Figs 5–8.

The thermal decomposition of $Ni(NCS)_2py_2$ is a one-step process, the maximum decomposition rate being at 259°; this is in agreement with the results in papers [21–23]. Bowman and Rogers [24] and Majumdar and co-workers [26] found that the complex $Ni(NCS)_2py$ was formed, but in the present work this was not observed.

The thermal decomposition of $Ni(NCS)_2(\beta\text{-pic})_2$ exhibits two steps, the decomposition rates reaching their maxima at 205° and 242°, respectively. These results are in agreement with the data in [25]. In the decomposition of $Ni(NCS)_2(\beta\text{-pic})_4$

Majumdar and co-workers [26] did not observe the formation of $Ni(NCS)_2(\beta\text{-pic})_2$; $Ni(NCS)_2(\beta\text{-pic})$ was obtained directly. This is in contrast with the present results.

The diffuse reflectance spectrum of $Ni(NCS)_2(\beta\text{-pic})$ (Fig. 4, B) in the visible region shows a combined absorption band with a maximum at 15.50 kK (645 nm) and a shoulder at 14.50 kK (690 nm); these may be assigned to the transitions $^3B_{1g} \rightarrow {}^3E_{g(F)}$ and $^3B_{1g} - {}^3A_{2g}$, respectively, in the weak field of tetragonal symmetry D_{4h}, analogously as for isomer *II* [6]. The coordination numbers of the complexes formed in the thermal decomposition of $Ni(NCS)_2(\beta\text{-pic})_2$ remain unchanged.

The thermal decompositions of the square-planar $Ni(NCS)_2(\alpha\text{-pic})_2$ [7] and $Ni(NCS)_2(2,6\text{-lut})_2$ proceed in one step with maximum decomposition rates at 165° and 199°, respectively. The found loss of weight values are in good agreement with those calculated. The diffuse reflectance spectrum of the complex $Ni(NCS)_2(2,6\text{-lut})_2$ (Fig 4, C) (an intense band at 550 nm), which is analogous to those of the complexes $Ni(NCS)_2(\alpha\text{-pic})_2$ [7] and $Ni(NCS)_2Q_2$ (*I*), enables us to propose a square-planar configuration for this complex too.

III. With complexes of the type $Ni(NCS)_2L_2$ (L = py; α-pic; β-pic; 2,6-lut, and Q), the volatile ligands have been found to leave either in one step according to the scheme:

$$Ni(NCS)_2L_{2(s)} \rightarrow Ni(NCS)_{2(s)} + 2L_{(g)} \qquad \text{(A)}$$

or in two steps:

$$Ni(NCS)_2L_{2(s)} \rightarrow Ni(NCS)_2L_{(s)} + L_{(g)} \rightarrow Ni(NCS)_{2(s)} + 2L_{(g)} \qquad \text{(B)}$$

The found stepwise character of the thermal decompositions is shown in Table 2 in relation to the geometrical configurations of the initial complexes.

Table 2

Compound	Colour	Geometrical configuration	Stoichiometric decomposition
$Ni(NCS)_2py_2$ $Ni(NCS)_2(\beta\text{-pic})_2$ $Ni(NCS)_2Q_2$ (*II*)	Green	Tetragonal-bipyramidal	One step Two steps One step
$Ni(NCS)_2(\alpha\text{-pic})_2$ $Ni(NCS)_2(2,6\text{-lut})_2$ $Ni(NCS)_2Q_2$ (*I*)	Red	Square-planar	One step One step Two steps

So far, the problems of the different stoichiometric decompositions of complexes of the same type as a whole have not been studied. Most authors report merely a certain stoichiometric decomposition. Liptay [27], however, tried to find the answer to this problem, i.e. the possible reasons for the two-step decomposition of the complex $Ni(NCS)_2py_4$. On the basis of differences in the C–C and C–H deformation vibrations of the coordinated py molecules in the infrared spectrum [22, 27], he suggests that even in the initial complex the two pyridine molecules are not equivalent. It does not seem probable, however, that these differences could cause such expressed changes in the strength of the pyridine ligand N–Ni bond.

Neither does the structures of this complex, determined by means of X-ray structural analysis [28], show the pyridine molecules to be energetically inequivalent, or bonded in two different ways. This factor may play an important part if one molecule of the volatile component is in the coordination sphere, the other being in the crystal lattice, e.g. in $Cu(H_2O)_4SO_4 \cdot H_2O$, where the two-step decomposition may be expected. Some authors have even found a three-step decomposition. It has been shown that even such physical properties of the microcrystalline product as the thickness of the layer [29] and the size of the crystals, the temperature of the isothermal decomposition [30], and the rate of temperature increase for non-isothermal conditions [31] influence the stoichiometry of decomposition. This may explain why different authors have different views on the stoichiometry of decomposition of a given complex. This factor, however, need not be taken into account for the $Ni(NCS)_2L_2$ complexes under investigation since all these complexes were decomposed under the same physical conditions (the same rate of temperature increase, the same sample weight, the same crystal size, almost the same layer thickness, the same defined atmosphere). Neither do the measured infrared absorption spectra nor the published data [32] reveal that the volatile ligands in complexes of the type $Ni(NCS)_2L_2$ are bonded in a different way.

In a study of these questions for complexes of the same type, the influence of the geometrical configurations of the initial complexes has also to be considered. When a complex with a coordination number of 5 is produced upon the release of the first molecule from a pseudo-octahedral complex of the type $Ni(NCS)_2L_2$ (L = unidentate volatile ligand), followed on the release of the other molecule by the formation of a complex with a coordination number of 4, no change of the crystal lattice must occur. The stepwise occurrence of the process then depends on the stabilities of the compounds with coordination numbers 5 and 4, respectively. In the present case, however, the final product is $Ni(NCS)_2$ with pseudo-octahedral configuration, excluding the coordination number 4.

Since the coordination number 6 does not change in the course of the decomposition for the pseudo-octahedral complexes under investigation, a reorganization of the crystal lattice must take place. The same applies for square-planar complexes, where the coordination number increases. The formation of new crystal lattice nuclei must be taken into account here, and also the rates of their formation and growth.

If the geometrical configuration influences the stepwise character of the thermal decomposition, different decomposition stoichiometries may be expected for the case when starting complexes of the same type have different geometrical configurations and the final products are the same compound. Though different decomposition stoichiometries were found for the isomers of $Ni(NCS)_2Q_2$ (Table 2), for the pseudo-octahedral isomer (*II*) the decomposition takes place in one step, while $Ni(NCS)_2 \cdot (\beta\text{-pic})_2$ of the same configuration gives rise to two steps. Equally, one-step decomposition was found too for the square-planar complexes of $Ni(NCS)_2(\alpha\text{-pic})_2$ and $Ni(NCS)_2(2,6\text{-lut})_2$, whereas for the square-planar isomer (*I*) it was a two-step process. This excludes any direct relationship between the geometrical configurations of the starting complexes of the type $Ni(NCS)_2L_2$ and the stoichiometries of their thermal decompositions.

Thus, it can be seen that the stoichiometry of the thermal decomposition of a complex is influenced not only by chemical factors such as the structures of the complex, but also by the physical conditions of the experiments, and by thermodynamic and kinetic factors. Only the complex investigation of all the above factors for every system studied can lead to the elucidation of the real reasons for the different stoichiometries of thermal decompositions and of the mechanisms.

These considerations have led us to study in our further work the thermochemical properties and the decomposition kinetics of complexes of the type $Ni(NCS)_2L_2$.

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RÉSUMÉ — Etude de la décomposition thermique des complexes solides de formule générale $Ni(SCN)_2L_2$ (L = pyridine, α-picoline, β-picoline, lutidine-2,6 et quinoléine) à l'aide du "Derivatograph". La décomposition des complexes de la pyridine, l'α-picoline, la lutidine-2,6 et la quinoléine (complexes pseudo-octaédriques) se déroule en une seule étape, tandis que celle des complexes de la β-picoline et de la quinoléine (complexes plans carrés) s'effectue en deux temps. Emploi des spectres de réflexion diffuse pour élucider la structure des produits intermédiaires de la décomposition. Interprétation des différences de stoechiométrie pendant la décomposition des complexes du même type.

ZUSAMMENFASSUNG — Die festen Komplexverbindungen $Ni(NCS)_2L_2$ (L = Pyridin, α- und β-Picolin, 2,6-Lutidin und Chinolin) wurden derivatographisch untersucht. Die Komplexe mit Pyridin, α-Picolin, 2,6-Lutidin und Chinolin (pseudooktaedrische Komplexe) zerfallen in einer Stufe, die entsprechenden Verbindungen mit β-Picolin und Chinolin (quadratisch-planare Komplexe) in zwei Stufen. Die Strukturbestimmung der intermediären Zersetzungsprodukte wurde mit Hilfe der diffusen Reflexionsspektren durchgeführt. Die Ursachen der verschiedenen Zersetzungsstöchiometrien der Komplexe von gleichem Typ wurden diskutiert.

Резюме — С помощью дериватографа изучен термораспад твердофазных комплексов типа $Ni(NCS)_2L_2$ (L = пиридин, α-пиколин, β-пиколин, 2,6-лутидин и хинолин). Установлено, что распад комплексов с пиридином, α-пиколином, 2,6-лутидином и хинолином (псевдо-октаэдрический комплекс) является одноступенчатым процессом, а распад комплексов с β-пиколином и хинолином (планарный комплекс) — двухступенчатым. Для выяснения структуры промежуточных продуктов распада измерен спектр диффузионного отражения. Обсуждается причина различной стехиометрии распада в случае комплексов аналогичного типа.