Journal of Thermal Analysis, Vol. 7 (1975) 551–560

HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES.

VIII. STUDY OF THE STOICHIOMETRY OF THERMAL DECOMPOSITION OF NICKEL(II) COMPLEXES WITH AMMONIA

E. Jóna, T. Šramko and J. Gažo

Department of Inorganic Chemistry,
Slovak Technical University, Bratislava, Czechoslovakia

(Received December 1, 1973)

The influence of different modes of preparation on the stoichiometry of thermal decomposition of isothiocyanatonickel(II) complexes with ammonia was studied. It was found that the complex $Ni(NCS)_2(NH_3)_4$ (I) prepared by heterogeneous reaction undergoes decomposition in two steps ($-2\,NH_3$, $-2\,NH_3$), while for complex II, of the same composition but prepared by homogeneous reaction from solution, the decomposition proceeds in three steps ($-1\,NH_3$, $-1\,NH_3$, $-2\,NH_3$). Electronic and infrared absorption spectra were used for the study of the spectral properties of the starting complex. It was found that the different stoichiometries of thermal decompositions of complexes I and II do not cause differences in the bonding strength of the ammonia molecules (chemical factor); this effect is rather brought about by physical factors such as different imperfections of the crystal lattice.

In investigating the relationship between the reactivity and the structure of coordination compounds in the solid state, we earlier studied the influence of certain chemical factors (the shape of the coordination polyhedron, the presence of volatile ligands in the primary or secondary coordination sphere) and physical factors (particle size) on the stoichiometry of thermal decomposition of solid nickel(II) complexes [1–3]. We directed our attention above all to isomeric compounds, which are especially suitable for this study [4].

For Ni(II) the formation of configuration isomers differing in the shape of their coordination polyhedra appears to be characteristic [5–8], though for this central atom the classical types of isomerism are also known [9, 10].

In the present work we studied the effects of different modes of preparation of solid coordination compounds of the same composition on the stoichiometry of their thermal decomposition. As starting compounds isothiocyanatonickel(II) complexes with ammonia were used, for which some X-ray structural data are known [11, 12]. The processes applied were those proved satisfactory in the preparation of isomers [7–9].

Thus, this work also represents a contribution to the study of the isomerism of nickel(II) complexes in the solid state.

Experimental

Chemicals and analytical methods

$NiCl_2 \cdot 6H_2O$ (anal. grade), KNCS (anal. grade) and NH_3 (anal. grade) (Lachema) were used. $Ni(NCS)_2$ was prepared by thermal decomposition of $Ni(NCS)_2py_4$.

Nickel contents were determined complexometrically which was made according to the methods in paper [13].

Preparation of the compounds

$Ni(NCS)_2(NH_3)_4$ (I): A thin layer of $Ni(NCS)_2py_4$ was treated with gaseous ammonia from a cylinder, or the solid complex was placed into an exsiccator near a bowl containing an aqueous solution of ammonia, to constant weight. The composition of the compound formed corresponded to $\approx Ni(NCS)_2(NH_3)_{5.5}$. This product lost about 1.5 mole ammonia and changed at room temperature to the complex $Ni(NCS)_2(NH_3)_4$ (I). The increase and loss of weight were followed by weighing. The same result was obtained when $Ni(NCS)_2$ was used as starting compound.

$Ni(NCS)_2(NH_3)_4$ (II); $NiCl_2 \cdot 6H_2O$ (0.04 mole) was dissolved in ethanol (80 ml) under stirring. After dissolution, solid ground KNCS (0.08 mole) was added. The separated KCl was filtered off and a 25% aqueous solution of ammonia (12 ml) was added to the pure solution of $Ni(NCS)_2$. After about two days dark blue crystals separated, which were washed with ethanol and air-dried.

Analysis

Calculated for $Ni(NCS)_2(NH_3)_4$: 24.16% Ni; 28.00% NH_3;
Found for complex I: 23.80% Ni; 27.88% NH_3;
Found for complex II: 23.80% Ni; 27.87% NH_3.

Apparatus

The thermal decomposition was studied by means of a Derivatograph (MOM Budapest). The apparatus and its operation are explained in paper [14]. Platinum crucibles with an upper diameter of 14 mm were used, and the thermocouples were Pt/Pt-Rh. All the powder samples, of 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 air atmosphere.

The powder diffractograms of the samples under investigation were taken with a GON III diffractograph (Chirana), automatically recording the diffracted radiation. The radiation used was CuK_α.

The electron absorption spectra of the solid samples were measured in Nujol with a SPECORD spectrophotometer (Zeiss, Jena).

The infrared absorption spectra of the powder samples in Nujol were taken with a double-beam UR-10 spectrophotometer (Zeiss, Jena) in the range 400–4000 cm^{-1}; below 400 cm^{-1} a Perkin-Elmer 225 spectrophotometer was used.

Results and discussion

In studying the influence of certain factors on the stoichiometry of thermal decomposition of solid nickel(II) complexes, we directed our attention to the question of whether different modes of preparation can have any influence, since it is known that this factor can play a considerable role in the kinetics of reactions in the solid state [15]. We applied the combination of homogeneous reactions (water-alcohol solution) with heterogeneous ones for the preparation of the starting complexes, which then were subjected to thermal decomposition. Thermoanalytical methods (DTA, DTG and TG) were used in the investigation.

A/ Thermal properties of complexes I and II

The DTA, DTG and TG curves of the complexes $Ni(NCS)_2(NH_3)_4$ (I and II) (Figs 1 and 2) lead to the following conclusions:

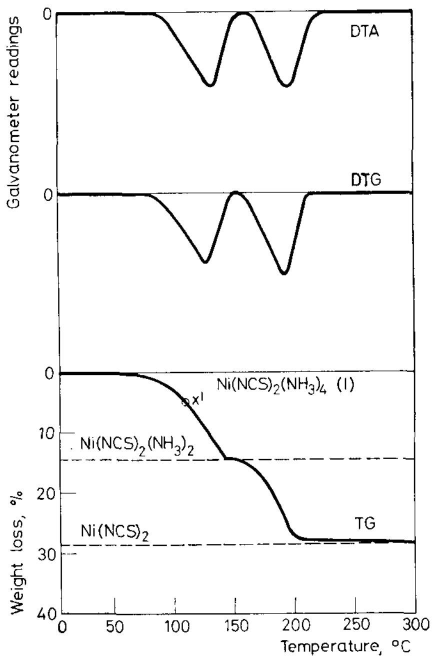

Fig. 1. Thermal curves of complex I

Up to 65° complexes I and II show constant weight. The thermal decomposition of complex I takes place in two separate steps, whereas that of complex II needs three. The weight losses corresponding to the decomposition stages are for complex I: 14.5% and 28.5%, respectively; and for complex II: 7.5%, 14.5% and 28.5% respectively. These results are in good accordance with the theoretical values: $-1\ NH_3$: 7.0%; $-2\ NH_3$: 14.0%; $-4\ NH_3$: 28.1%. The decomposition rate maxima for the studied processes are at 125 and 195°, for complex I, and at 125, 160 and 200° for complex II. As the DTA curves show, only endothermic processes are involved in the decomposition.

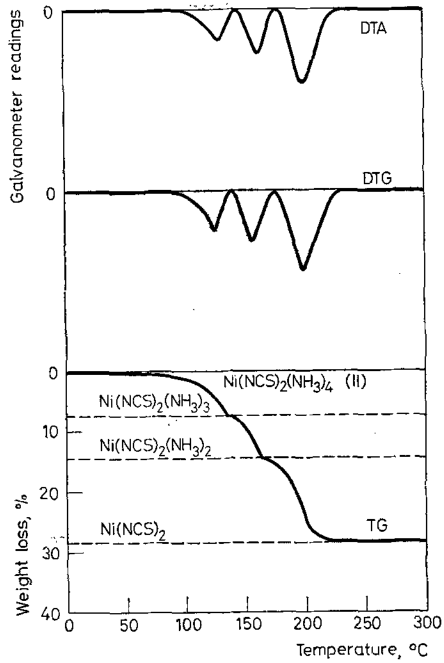

Fig. 2. Thermal curves of complex II

The stoichiometry of the thermal decomposition of complex I may be expressed by equations (1) and (2):

$$Ni(NCS)_2(NH_3)_{4(s)}\ (I) \rightarrow Ni(NCS)_2(NH_3)_{2(s)} + 2NH_{3(g)} \tag{1}$$

$$Ni(NCS)_2(NH_3)_{2(s)} \rightarrow Ni(NCS)_{2(s)} + 2NH_{3(g)} \tag{2}$$

and that of complex II by equations (3)–(5):

$$Ni(NCS)_2(NH_3)_{4(s)}\ (II) \rightarrow Ni(NCS)_2(NH_3)_{3(s)} + NH_{3(g)} \tag{3}$$

$$Ni(NCS)_2(NH_3)_{3(s)} \rightarrow Ni(NCS)_2(NH_3)_{2(s)} + NH_{3(g)} \tag{4}$$

$$Ni(NCS)_2(NH_3)_{2(s)} \rightarrow Ni(NCS)_{2(s)} + 2NH_{3(g)} \tag{5}$$

Thus, the stoichiometries of thermal decomposition of complexes I and II differ; this may be connected with structural differences in the primary coordination sphere. These differences in thermal decomposition led us to study the spectral properties of these compounds.

B/ Spectral properties of complexes I and II in the solid state

The electron absorption spectra of the coordination compounds under investigation exhibit two bands in the measured range (14 000 – 30 000 cm^{-1}), with maxima at ≈17 000 cm^{-1} and 28 000 cm^{-1}, respectively (Table 2). Based on these data and in accord with the results of magnetochemical measurements [16] (complex II: $\mu_{eff} = 3.28$ B.M.) these compounds may be considered paramagnetic complexes with pseudooctahedral configuration. The assumed environment $NiN'_4N''_2$ for complexes I and II and also X-ray structural analysis of complex II [11] indicate tetragonal distortion of these compounds, causing a lowering of the symmetry from O_h to D_{4h} [17] (three absorption bands are split into six). Actually, as supported by our experiments, all six bands are to be observed only rarely.

Table 1

Spectral data for isothiocyanatonickel (II) complexes with ammonia (in cm^{-1})

Compound	Spectral data	
	Visible region	Infrared region
I	28 000 17 150	3360, 3270, 2108, 1618, 1212 785, 612, 477, 330, 210–200
II	28 000 17 150	3358, 3267, 2105, 1618, 1210, 785, 606, 477, 330, 210–200

The absorption bands with maxima at 17 000 cm^{-1} and 28 000 cm^{-1} are only very little distorted, so that without analysis of the spectral curves it appears impossible even approximately to determine the values of the maxima of the respective bands. We have therefore listed in Table 1 the values of the maxima formed by superposition of two bands. The experimental data obtained for the complexes $Ni(NCS)_2(NH_3)_4$ agree well with the calculated values [17]. As Table 1 shows, no differences were observed between the electronic spectra of complexes I and II.

The infrared absorption spectra of the complexes under investigation exhibit 10 – 13 bands in the measured range (200 – 4000 cm^{-1}) (Table 1). The bands typical of the coordinated ammonia molecules are at 3360 and 3260 cm^{-1}, respectively (asymmetrical and symmetrical valence vibrations of NH_3), at 1600 and 1200 cm^{-1}, respectively (asymmetrical and symmetrical deformation vibrations of NH_3) and at 600 cm^{-1} ("rocking" vibrations of NH_3). It follows from these results, and also from literature data [18–20], that all the ammonia molecules are coordinated to the Ni(II) atom.

For the NCS group those bands are characteristic that correspond to the valence vibrations of C–N (at ≈ 2100 cm^{-1}) and of C–S (at ≈ 780 cm^{-1}), and to the deformation vibration of the NCS group (at ≈ 475 cm^{-1}). In accordance with literature data [7, 11, 21, 22], Table 2 shows that for complexes I and II the NCS group appears end bonded through the N atom, since the absorption band in the interval 690–730 cm^{-1}, known for the coordination of M–SCN, is missing [21].

In the region under 400 cm^{-1} there occur the bands $\bar{\nu}_{Ni-N(NH_3)}$ and $\bar{\nu}_{Ni-N(NCS)}$ (in addition to δ_{N-Ni-N}), giving direct information on the character of the metal-ligand bonds. In interpreting the results obtained we relied upon the work of Viltange [23], who found the Ni–NH$_3$ vibration bands in the range 317–344 cm^{-1} and the δ_{N-Ni-N} bands at 214–224 cm^{-1}, respectively, for the complexes $Ni(NH_3)_6X_2$ (X = Cl, Br, I). For complexes of $[Ni(NCS)_6]^{-4}$ Forster and Goodgame [24] observed the Ni–N(NCS) vibration bands in the range 237–250 cm^{-1}. Paper [22] deals with this problem as a whole.

The band at 330 cm^{-1} corresponding to the Ni–N(NH$_3$) vibration indicates that all ammonia molecules are energetically equivalent for both complexes I and II. The broad band at 210–200 cm^{-1} apparently involves the two remaining vibrations $\nu_{Ni-N(NCS)}$ and δ_{N-Ni-N}.

C/ Causes of the different stoichiometries of decomposition for complexes I and II

In studying the influence of the different modes of preparation of the complexes on the stoichiometries of their thermal decomposition, we tried to prepare two differently distorted octahedral complexes $Ni(NCS)_2(NH_3)_4$. Complex II exhibits a tetragonal bipyramidal structure with the interatomic distances [11] $d_{Ni-N(NH_3)} = 2.15(\pm 0.02)$ Å and $d_{Ni-N(NCS)} = 2.07(\pm 0.03)$ Å, i.e. the tetragonal bipyramid has a compressed form. The complex $Ni(NCS)_2(py)_4$ also has a tetragonal bipyramidal coordination polyhedron, but the interatomic distances [16, 25] are different: $d_{Ni-N(py)} = 2.03(\pm 0.06)$ Å and $d_{Ni-NCS} = 2.12(\pm 0.03)$ Å, these meaning that the tetragonal bipyramid is elongated. By applying the heterogeneous reaction of solid $Ni(NCS)_2(py)_4$ with gaseous ammonia we attempted to prepare the complex $Ni(NCS)_2(NH_3)_4$ with a coordination polyhedron in the shape of an elongated tetragonal bipyramid. Though the infrared spectra, particularly in the region of direct central atom – ligand interactions (under 400 cm^{-1}), did not confirm this conception, different stoichiometries of thermal decomposition of these complexes were observed.

Since the complexes I and II did not show any differences in the strengths of the Ni–N(NH$_3$) bonds, the reasons for their different decomposition stoichiometries have to be sought rather in physical factors connected with their crystal structures. A possible explanation might lie in the different degrees of defectiveness of the crystals. Complex II, prepared by crystallization from solution, exhibits more regularly grown crystals, offering greater resistance to the diffusivity of ammonia, so that the formation of the intermediate $Ni(NCS)_2(NH_3)_3$ is favoured. Complex I, 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 $Ni(NCS)_2(NH_3)_2$ is formed directly.

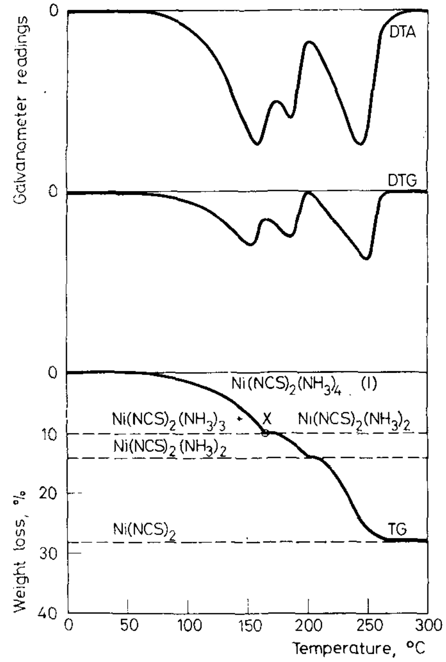

Fig. 3. Thermal curves of complex I: sample of 400 mg, compressed

The above conceptions are also supported by the fact that if we increase the sample of complex I and compress it, the resistance to diffusion and also the ammonia concentration in the reaction interphase are both increased, and the thermoanalytical curves show (Fig. 3) an intermediate x, for which the loss of weight does not correspond exactly, however, to the loss of one mole NH_3; nevertheless, the diffractogram of x (Fig. 4/A) exhibits lines corresponding to the complexes $Ni(NCS)_2(NH_3)_3$ (Fig. 4/B) (prepared by thermal decomposition of complex II) and $Ni(NCS)_2(NH_3)_2$ (Fig. 4/C). The intermediate $Ni(NCS)_2(NH_3)_3$ was also observed when complex I underwent thermal decomposition about six months after its preparation, when recrystallization had taken place, in the solid phase thereby decreasing the defectiveness of the structure. In the decomposition of a thin layer of freshly prepared complex I (intermediate x' in Fig. 1) the complex $Ni(NCS)_2(NH_3)_3$ was not observed; even phase analysis (Fig. 4/D) showed the only complex formed to be $Ni(NCS)_2(NH_3)_2$. The powder diffractogram of the intermediate x' exhibits lines corresponding to the complexes $Ni(NCS)_2(NH_3)_4$ and $Ni(NCS)_2(NH_3)_2$. It follows from the above that it is desirable to complete the study of the stoichiometry of thermal decomposition by the phase analysis of the intermediates.

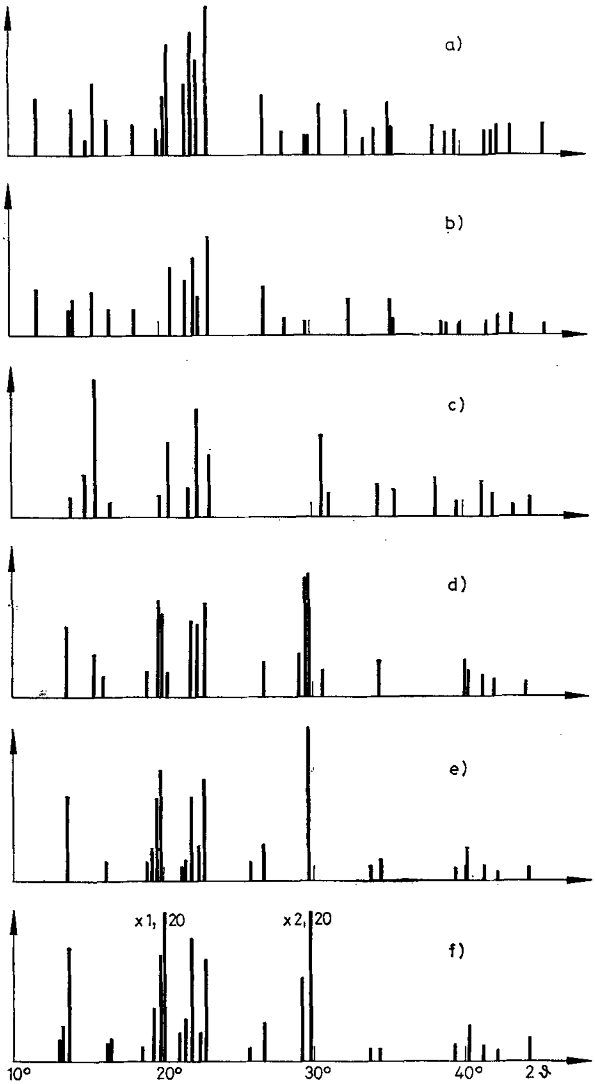

Fig. 4. Powder diffractograms: a — intermediate x (see Fig. 3); b — $Ni(NCS)_2(NH_3)_3$; c — $Ni(NCS)_2(NH_3)_2$; d — intermediate x' (see Fig. 1); e — complex I; f — complex II

The powder diffractograms of complexes I and II (Figs 4/E and 4/F) show fine shifts of some bands; the band at ~29° is split into two and on transition to complex II an intensive increase in the intensity of the most characteristic bands is found. It cannot be excluded, however, that these changes are due to different defects of the crystal lattice, i.e. to different mosaics of the crystal structures of complexes I and II, thus affecting the stoichiometries of their thermal decomposition.

References

1. E. JÓNA, T. ŠRAMKO and J. GAŽO, J. Thermal. Anal., 4 (1972) 61.
2. E. JÓNA, T. ŠRAMKO and J. GAŽO, Chem. Zvesti, 27 (1973) 145.
3. T. ŠRAMKO and E. JÓNA, Coll. Czech. Chem. Commun., 37 (1972) 1645.
4. F. BASOLO and R. G. PEARSON, Mechanism of Inorganic Reactions; Russian translation: Mechanizmy neorganiceskich reakcij, Izd. MIR, Moscow, 1971, p. 220.
5. T. ŠRAMKO, E. JÓNA and A. SIROTA, Proceedings of the 2nd Conference on Coordination Chemistry, Smolenice-Bratislava, 1969, p. 239.
6. A. V. DOWNS and D. A. ONGLEY, Chem. Ind., 23 (1963) 493.
7. E. JÓNA, T. ŠRAMKO, J. KOHOUT, A. SIROTA and J. GAŽO, Chem. Zvesti, 25 (1971) 241.
8. E. JÓNA, M. JAMNICKÝ, T. ŠRAMKO and J. GAŽO, Coll. Czech. Chem. Commun., 37 (1972) 3679.
9. A. SIROTA, E. JÓNA and T. ŠRAMKO, Proceedings of the 13th International Conference on Coordination Chemistry, Crakow—Zakopane, Poland 1970, p. 356.
10. E. JÓNA, T. ŠRAMKO and J. GAŽO, Chem. Zvesti, 27 (1973) 145.
11. E. K. YUKHNO and M. A. PORAI-KOSHITZ, Kristallografiya, 2 (1957) 239.
12. M. A. PORAI-KOSHITZ, S. A. ANTSISHKINA, L. M. DIKAREVA and E. K. YUKHNO, Acta Cryst., 10 (1957) 784.
13. E. JÓNA, T. ŠRAMKO and J. GAŽO, Chem. Zvesti, 22 (1968) 648.
14. F. PAULIK, J. PAULIK and L. ERDEY, Z. anal. Chem., 160 (1958) 241.
15. C. M. E. GARCIA and M. F. BURRIEL, Rev. port. juim., 13 (1971) 1.
16. M. A. PORAI-KOSHITZ, Zh. Neorg. Khim., 4 (1959) 730.
17. A. B. P. LEVER, Coord. Chem. Rev., 3 (1968) 129.
18. G. F. SVATOS, D. M. SWEENY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, J. Am. Chem. Soc., 79 (1957) 3313.
19. E. P. BERTIN, I. NAKAGAWA, S. MIZUSHIMA, T. J. LANE and J. V. QUAGLIANO, J. Am. Chem. Soc., 80 (1958) 525.
20. K. NAKAMOTO, Infrared spectra of Inorganic and Coordination Compounds. J. Wiley, Inc. New York—London 1963, p. 143.
21. M. A. PORAI-KOSHITZ and G. V. TSINADZE, Kristallokhim, (1965), Itogi Nauki, Ser. Chim., Moscow 1967, p. 168.
22. R. A. BAYLEY, S. L. KOZAK, T. W. MICHELSEN and W. N. MILLS, Coord. Chem. Rev., 6 (1971) 407.
23. M. VILTANGE, Mikrochim. Acta (Wien), (1965) 609.
24. D. FORSTER and D. M. L. GOODGAME, Inorg. Chem., 4 (1965) 715.
25. M. A. PORAI-KOSHITZ, E. K. YUKNO, A. S. ANTSISKHINA and L. M. DIKAREVA, Kristallografiya, 2 (1957) 371.

RÉSUMÉ — On a étudié l'influence des diverses méthodes de préparation sur la stoechiométrie de la réaction de décomposition thermique des complexes de l'isothiocyanate de nickel(II) avec l'ammoniac. On a établi que le complexe $Ni(SCN)_2(NH_3)_4$, (I), préparé par réaction hétérogène, subit une décomposition en deux étapes ($-2NH_3$, $-2NH_3$), tandis que le complexe (II), de même composition, mais préparé par réaction homogène, à partir de solutions, se décompose en trois étapes ($-1NH_3$, $-1NH_3$, $-2NH_3$). Les propriétés spectrales du complexe initial ont été étudiées par absorption électronique et infrarouge. On a trouvé que les différences de stoechiométrie des réactions de décomposition thermique des complexes (I) et (II) n'apportaient pas de différences entre les énergies de liaison des molécules d'ammoniac (facteur chimique). C'est plutôt à des facteurs physiques, comme les différentes imperfections du réseau cristallin, que cet effet serait dû.

ZUSAMMENFASSUNG — Der Einfluß der Herstellung auf die Stöchiometrie der thermischen Zersetzung von Amin-Komplexen des Isothiocyanatonickels wurde studiert. Der Zerfall des Komplexes $Ni(NCS)_2(NH_3)_4$ (I), hergestellt durch heterogene Reaktion, verlief in zwei Etappen ($-2\,NH_3$, $-2\,NH_3$). Beim selben Komplex (II), hergestellt durch homogene Reaktion in Lösung, wurden jedoch drei Etappen beobachtet ($-1\,NH_3$, $-1\,NH_3$, $-2\,NH_3$). Die Eigenschaften des Ausgangsproduktes wurden durch Elektronen- und IR-Spektroskopie untersucht. Das unterschiedliche thermische Verhalten ist nicht auf eine verschiedene Bindungsstärke der NH_3 Moleküle, sondern auf physikalische Ursachen, wie z. B. Unregelmässigkeiten im Kristallgitter zurückzuführen.

Резюме — Изучено влияние различных методов получения аммиачных комплексов изотиоцианата никеля (II) на стехиометрию их термического разложения. Было найдено, что комплекс $Ni(NCS)_2(NH_3)_4$ (I), полученный при гетерогенной реакции, подвергается двухступенчатому разложению ($-2NH_3$,$-2NH_3$). В то же время, для комплекса II того же состава, но полученного при гомогенной реакции из растворов, разложение протекает в три стадии ($-1\,NH_3$,$-1\,NH_3$ $-2NH_3$). Для изучения спектральных свойств начальных комплексов были использованы электронные и инфракрасные спектры поглощения. Найдено, что различная стехиометрия термического разложения комплексов I и II обусловлена не различием в силе связи молекул аммиака (химический фактор), а скорее всего физическими факторами, такими как различные дефекты их кристаллической решетки.