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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES. XVIII*

Stoichiometry of thermal decomposition and stereochemistry of compounds $Ni(NCS)_2(2\text{-}R\text{-}pyridine)_n$ (R = Me, Et, Cl, Br, NH_2) and their decomposition products

E. Jóna and *M. Jamnický*

DEPARTMENT OF INORGANIC CHEMISTRY, SLOVAK TECHNICAL UNIVERSITY,
812 37 BRATISLAVA, CZECHOSLOVAKIA

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The stoichiometry of thermal decomposition was studied for the following compounds:

$Ni(NCS)_2(2\text{-}Mepy)_2$ (I), (Me = methyl, py = pyridine),

$Ni(NCS)_2(2\text{-}Etpy)_2$ (II) (Et = ethyl),

$Ni(NCS)_2(2\text{-}Clpy)_2$ (III), $Ni(NCS)_2(2\text{-}Brpy)_2$ (IV),

$Ni(NCS)_2(2\text{-}NH_2py)_4$ (V), $Ni((NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\,(C_2H_5)_2O$ (VI).

The release of volatile ligands 2-Rpy is a one-step process for complexes I, II, III and IV, while for V and VI it is a two-step process, $Ni(NCS)_2(2\text{-}NH_2py)_1$ (VII) being formed as an intermediate complex. It was found that complexes I and II are square-planar; the others exhibited pseudo-octahedral geometry. The differences in stereochemistry of the above complexes are explained by the different electronic properties of 2-Rpy.

The stoichiometry (stepwise character) of thermal decomposition of solid nickel(II) complexes generally depends on various factors [1]: their crystal structure, the experimental conditions in the measurements, as well as the properties of the ligands (electronic and steric) and their mutual interactions. The position and nature of substituents in the ligands may play a great role; they influence the stereochemistry of the starting complexes (and also the products formed by decomposition) and moreover the stoichiometry of thermal decomposition.

From the above aspect, our study was oriented to isothiocyanate complexes with monosubstituted pyridines (Rpy). In previous papers we have dealt with compounds

$Ni(NCS)_2(4\text{-}Rpy)_n$ [2] and $Ni(NCS)_2(3\text{-}Rpy)_n$ [3].

In this paper we have studied the influence of a substituent in position 2 (α-position) on the composition, the stoichiometry of thermal decomposition and the stereochemistry of compounds $Ni(NCS)_2(2\text{-}Rpy)_n$ (R = Me, Et, Cl, Br, NH_2).

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Experimental

Preparation of starting compounds

The preparation and thermal properties of $Ni(NCS)_2(2\text{-}Mepy)_2$ (I) are described in papers [4, 5].

$Ni(NCS)_2(2\text{-}Etpy)_2$ (II): 80 cm^3 of an ethanolic solution containing 0.04 mole of $Ni(NCS)_2$ was mixed with 0.16 mole of 2-Etpy and stirred. The red product which crystallized from the solution had the composition $Ni(NCS)_2(2\text{-}Etpy)_2$. It was washed with ether and air-dried. $Ni(NCS)_2(2\text{-}Clpy)_2$ (III) (green), $Ni(NCS)_2(2\text{-}Brpy)_2$ (IV) (green), and $Ni(NCS)_2(2\text{-}NH_2py)_4$ (V) (blue-green) were prepared analogously as complex II. Product III is not very stable in the air and partially decomposes at room temperature to yield yellow $Ni(NCS)_2$.

$Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\,(C_2H_5)_2O$ (VI): The finely ground complex V was treated under intense stirring for a long time with ether (0.01 mole was extracted ten times with 50 cm^3 portions of ether); the resulting air-dried pea-green product has a reproducible composition: $Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\,(C_2H_5)_2O$. The TG curve (Fig. 2) confirmed this composition. We did not succeed in preparing $Ni(NCS)_2(2\text{-}NH_2py)_2$ either from solution or by decomposition of complexes V and VI. (Compound VI seems to be stabilized by diethyl ether, which is involved in a polymeric system with polydentately bonded ligands.)

$Ni(NCS)_2(2\text{-}NH_2py)_1$ (VII) (green) was prepared by isothermal decomposition of complex VI at 120°.

Analytical methods and equipment

The analytical methods and equipment used were described in papers [6–8]. The samples for thermal decomposition always had a mass of 100 mg. The rate of temperature increase was 3 deg/min. Measurements were made in air atmosphere: a platinum polyplate crucible was used.

Results and discussion

Thermal properties

The TG, DTG and DTA curves permit the following conclusions: As concerns mass decrease, complexes I–VI are thermally stable up to 75, 70, 65, 105, 75 and 95°, respectively. The stability of complexes of the composition $Ni(NCS)_2(2\text{-}Rpy)_2$ increases approximately in the sequence: $Cl < Et < Me < Br$. The thermal stability of complex III is very low compared with those observed for complexes with the substituents 4-Rpy [2] and 3-Rpy [3]. The TG and DTG curves for complexes I, II, III and IV show that the release of the volatile ligands 2-Rpy is a one-step process according to the equation:

$$Ni(NCS)_2(2\text{-}Rpy)_{2(s)} \longrightarrow Ni(NCS)_{2(s)} + 2\,(2\text{-}Rpy)_{(g)} \qquad (R = Me, Et, Cl, Br)$$

The TG, DTG and DTA curves of complex I are given in paper [5], and those for complex IV in Fig. 1. Complexes II and III have analogous decomposition curves as found for complexes I and IV. However, the loss of ligands occurs in two steps for complexes V and VI (the TG, DTG and DTA curves for complex VI are given in Fig. 2):

$$Ni(NCS)_2(2\text{-}NH_2py)_4\ (V)_{(s)} \longrightarrow$$

$$\longrightarrow Ni(NCS)_2(2\text{-}NH_2py)_1\ (VII)_{(s)} + 3\ (2\text{-}NH_2py)_{(g)}$$

$$Ni(NCS)_2(2\text{-}NH_2py)_{1(s)} \longrightarrow Ni(NCS)_{2(s)} + (2\text{-}NH_2py)_{(g)}$$

and

$$Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\ (C_2H_5)_2O\ (VI)_{(s)} \longrightarrow$$

$$\longrightarrow Ni(NCS)_2(2\text{-}NH_2py)_1\ (VII)_{(s)} + (2\text{-}NH_2py)_{(g)} + 3/4\ (C_2H_5)_2O_{(g)}$$

$$Ni(NCS)_2(2\text{-}NH_2py)_{1(s)} \longrightarrow Ni(NCS)_{2(s)} + (2\text{-}NH_2py)_{(g)}$$

The existence of defined intermediates was proved by phase analysis (by means of X-ray powder patterns).

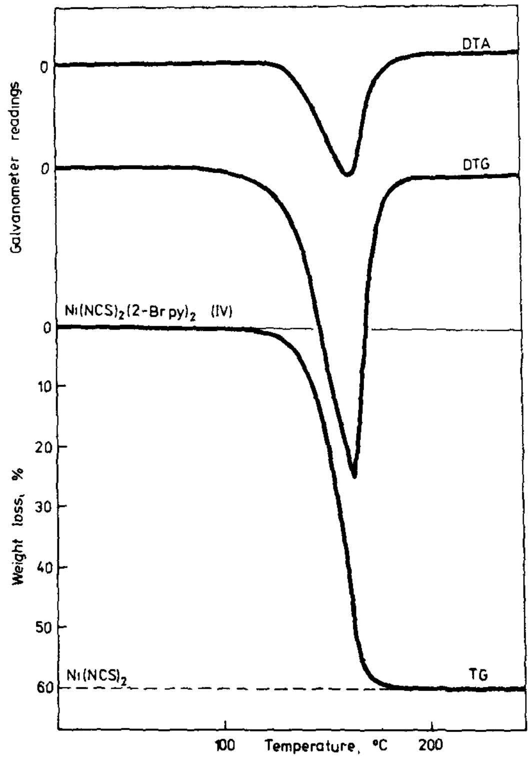

Fig. 1 Thermal curves of complex $Ni(NCS)_2(2\text{-}Brpy)_2$ (IV)

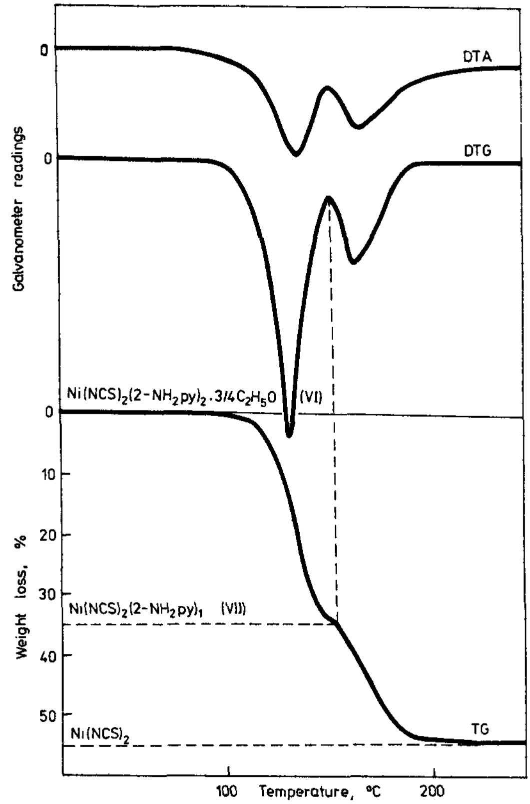

Fig. 2 Thermal curves of complex $Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\ (C_2H_5)_2O$ (VI)

Magnetic and spectral properties

The magnetic moments and spectral data are given in Table 2. It is seen that there are two groups of complexes differing in magnetic and spectral properties. The first group includes complexes I and II, and the second group the other complexes. The complexes of the first group exhibit small positive corrected molar susceptibilities (χ'_M). They are probably temperature-independent susceptibilities conditioned by the Zeeman effect of the second order. Consequently, complexes I and II can be considered as monomolecular square-planar species with a basic singlet state ${}^1A_{1g}$. This conclusion was supported by the spectral data. Electronic (*d—d*) spectra for the complexes of the first group exhibit a distinct band, with maximum at 19 800 cm^{-1} and 20 000 cm^{-1} for complexes I and II, respectively, i.e. in the spectral region which is usually assigned to the first of the three bands in the spectra of square-planar nickel(II) complexes [6—10]. The bands in the near ultraviolet region cannot be identified exactly because they are overlapped by charge-transfer bands or by those

Table 1 Analytical data for complexes $Ni(NCS)_2(2\text{-}Rpy)_n$

Complex		Ni, %		C, %		H, %		N, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Ni(NCS)_2(2\text{-}Mepy)_2$	(I)	16.26	16.32	46.54	46.17	3.91	3.78	15.52	15.67
$Ni(NCS)_2(2\text{-}Etpy)_2$	(II)	15.09	15.27	49.38	48.85	4.66	4.48	14.40	14.47
$Ni(NCS)_2(2\text{-}Clpy)_2$	(III)	14.61	14.47	35.86	35.56	2.01	1.85	13.94	13.50
$Ni(NCS)_2(2\text{-}Brpy)_2$	(IV)	11.96	11.98	29.36	29.05	1.64	1.60	11.41	11.37
$Ni(NCS)_2(2\text{-}NH_2py)_4$	(V)	10.65	10.73	47.93	47.54	4.39	4.30	25.40	25.24
$Ni(NCS)_2(2\text{-}NH_2py)_2$ · 3/4 $(C_2H_5)_2O$	(VI)	14.02	14.05	43.03	42.57	4.69	4.78	20.07	19.72
$Ni(NCS)_2(2\text{-}NH_2py)_1$	(VII)	21.83	22.18	31.24	30.65	2.25	2.10	20.83	20.22

Table 2 Values of magnetic moments and maxima of absorption bands in electronic (*d–d*) spectra and IR spectra for complexes $Ni(NCS)_2(2\text{-}Rpy)_n$

Complex		μ_{eff}, B.M.	Maxima of absorption bands				
			Electronic spectra, cm^{-1}			IR-spectra, cm^{-1}	
						ν_{C-N}	ν_{C-S}
$Ni(NCS)_2(2\text{-}Mepy)_2$	(I)	0.67		19800		2105	856
$Ni(NCS)_2(2\text{-}Etpy)_2$	(II)	0.89		20000		2113	851
$Ni(NCS)_2(2\text{-}Clpy)_2$	(III)	3.34	9300	15450	25500	2116 2134	792
$Ni(NCS)_2(2\text{-}Brpy)_2$	(IV)	3.31	7200 10100(sh)■	14900	25600	2115 2137	790
$Ni(NCS)_2(2\text{-}NH_2py)_4$	(V)	3.16	9500	15800	25000–26000	2084 2100	▲
$Ni(NCS)_2(2\text{-}NH_2py)_2$ · 3/4 $(C_2H_5)_2O$	(VI)	3.26	9350	15050	23000–25000	2099 2135	▲
$Ni(NCS)_2(2\text{-}NH_2py)_1$	(VII)	paramm.●	8500(br)■	14400	22500–24500	2099 2120 2128 2145	▲

■ sh – shoulder, br – broad; ● the obtained amount of sample was not sufficient for a precise measurement of μ_{eff}; ▲ overlaid by $2\text{-}NH_2py$ absorption

assigned to ligands. Similarly, one band was observed in the mentioned region for nickel(II) complexes with lutidine [6], quinoline [7] and lepidine [8]. The square-planar geometry of the complexes under study requires terminally-bonded NCS groups, which is in agreement with the infrared spectral results (Table 2).

The effective magnetic moments and the maxima of the absorption bands for the complexes of the second group are within the region usually found for paramagnetic pseudo-octahedral nickel(II) complexes [2, 3, 11]. Two absorption bands above 2100 cm^{-1} were observed in the infrared spectra of the complexes $Ni(NCS)_2(2\text{-}Rpy)_2$ (R = Cl, Br) and were assigned to ν_{C-N} vibrations. These bands occurred in the region usually given for terminal or bridging NCS groups [7, 12] (Ni-SCN and Ni-SCN-Ni, respectively). The absence of a band in the region 690–730 cm^{-1} (ν_{C-S}) excludes the possibility of a Ni-SCN bond. Since the bonding system SCN-Ni-NCS is non-linear, the molecular symmetry of all polymeric octahedral thiocyanate complexes requires a double vibration of ν_{C-N} [13].

Two bands, at 2099 cm^{-1} and 2133 cm^{-1}, for $Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\,(C_2H_5)_2O$ (VI) may be a sign of the presence of differently bonded NCS groups (terminal and bridging) and consequently differently bonded molecules of $2\text{-}NH_2py$ (as unidentate or bidentate ligands coordinated through the nitrogen atom of pyridine and also through the nitrogen atom of the NH_2 group) [14].

A very strong band at 2099 cm^{-1} for $Ni(NCS)_2(2\text{-}NH_2py)_1$ (VII) corresponds to terminally-bonded NCS groups. Bands at 2120, 2128 and 2145 cm^{-1}, however, show that polydentate thiocyanate groups (bi- or tridentate) cannot be excluded, evidently forming together with $2\text{-}NH_2py$ a polymeric system with a pseudo-octahedral configuration of Ni(II).

Complex $Ni(NCS)_2(2\text{-}NH_2py)_4$ (V) is the only species among the compounds $Ni(NCS)_2(2\text{-}Rpy)_n$ where $n > 2$. The vibration ν_{C-N} (Table 2) indicates a terminally-bonded NCS group. The band is split, due to distortion of the regular O_h symmetry and linearity; it may possibly be connected with other effects in the solid state [15]. A study of the vibrations $\nu_{Ni-N(NH_2py)}$ and $\nu_{Ni-N(py)}$ has proved [14] that the individual molecules of $2\text{-}NH_2py$ in compound V are bonded to the Ni(II) atom only through the nitrogen atom of the NH_2 group; this has the consequence that steric hindrance is lowered and four organic molecules can be bonded.

Composition and stereochemistry of complexes $Ni(NCS)_2(2\text{-}Rpy)_n$

The complexes under investigation decompose in one or two steps and volatile nitrogen ligands are released (2-Rpy). The stereochemistry of the starting compounds and of the defined decomposition products is given in Table 3: except for $R = NH_2$, all complexes with the composition $Ni(NCS)_2(2\text{-}Rpy)_2$ have been prepared in the solid state. They are octahedral or square-planar, depending on the substituent used. With the change in R (R = Me, Et, Cl, Br), the stereochemistry of the complexes also change, but the same stoichiometry of thermal decomposition is kept. 2-Alkyl derivatives of pyridine (but also dialkyl derivatives such as 2,4-, 2,5- and $2,6\text{-}Me_2py$ [6]) form complexes with square-planar geometry, while 2-Clpy and 2-Brpy give complexes with pseudo-octahedral configuration only. Although different steric effects of the substituents cannot be completely excluded (in spite of them all being in position 2 of the pyridine ring), an explanation for the above phenomenon can be found in the dif-

Table 3 Geometry of complexes $Ni(NCS)_2(2\text{-}Rpy)_n$
(sq — square-planar, o — octahedral)

R-py	*n*				
	4	3	2	1	0
2-Mepy	—	—	sq	—	o
2-Etpy	—	—	sq	—	o
2-Clpy	—	—	o	—	o
2-Brpy	—	—	o	—	o
$2\text{-}NH_2py$	o	—	—	o	o
	—	—	o*	o	o

$^*Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\ (C_2H_5)_2O$

ferent electronic properties of the neutral ligands (for instance, in different inductive effect *I* of the substituents) [9].

Alkyl substituents exhibit positive inductive effects (+ *I*), and consequently the basicity and σ-bonding ability of 2-alkylpyridines should be greater than those of halogenopyridines. These properties of 2-alkylpyridines are evidently sufficient for them to form stable square-planar, i.e. only tetra-coordinated complexes.

The negative inductive effects (— *I*) of the substituents Cl and Br cause a significantly lower electronic density on the N(py) atom, and consequently hexa-coordinated complexes are formed.

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Zusammenfassung — Die Stöchiometrie der thermischen Zersetzung folgender Verbindungen wurde untersucht:

$Ni(NCS)_2(2\text{-}Mepy)_2$ (I) (Me = Methyl, py = Pyridin),

$Ni(NCS)_2(2\text{-}Etpy)_2$ (II) (Et = Äthyl),

$Ni(NCS)_2(2\text{-}Clpy)_2$ (III), $Ni(NCS)_2(2\text{-}Brpy)_2$ (IV),

$Ni(NCS)_2(2\text{-}NH_2py)_4$ (V), $Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\ (C_2H_5)_2O$ (VI).

Das Entweichen des flüchtigen Ligands 2-Rpy ist ein einstufiger Vorgang für die Komplexen I, II, III und IV, wogegen es für V und VI ein zweistufiger Vorgang ist, wobei $Ni(NCS)_2(2\text{-}NH_2py)_1$ (VII) sich als intermediärer Komplex bildet. Die Komplexe I und II sind quadratisch; die anderen zeigten eine pseudooktaedrische Geometrie. Die Unterschiede in der Stöchiometrie der obigen Verbindungen werden durch die unterschiedlichen elektronischen Eigenschaften von 2-Rpy erklärt.

Резюме — *Изучена стехиометрия термического разложения ряда соединений*

$Ni(NCS)_2(2\text{-}Rpy)_2$,

где

Me = метил — (I), этил — (II), Cl — (III), Br — (IV) и $Ni(NCS)_2(2\text{-}NH_2py)_4$ (V),

а также

$Ni(NCS)_2(2\text{-}NH_2py)_2 \cdot 3/4\ (C_2H_5)_2O$ (VI).

Выделение летучих лигандов — 2-Rpy — является одноступенчатым процессом в случае комплексов I—IV, и двухступенчатым — в случае комплексов V и VI, приводя к образованию промежуточного соединения $Ni(NCS)_2(2\text{-}NH_2py)_1$, где во всех случаях py-пиридин. Найдено, что комплексы I и II являются плоскими квадратными, а остальные комплексы имеют псевдооктаэдрическую структуру. Различия в стереохимии изученных комплексов обьясняется различными электронными свойствами лиганда 2-Rpy.