

THE STOICHIOMETRY OF THE THERMAL DECOMPOSITION  
AND STEREOCHEMISTRY OF COMPLEX COMPOUNDS  
OF THE  $\text{Ni}(\text{NCS})_2(4\text{-R-PYRIDINE})_4$  TYPE  
AND THEIR DECOMPOSITION PRODUCTS\*

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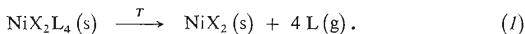
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Received August 16th, 1981

*Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.*

The stoichiometry of the thermal decomposition of the following compounds was studied:  $\text{Ni}(\text{NCS})_2(4\text{-EtPy})_4$  (*I*) (Et = ethyl, Py = pyridine),  $\text{Ni}(\text{NCS})_2(4\text{-ClPy})_4$  (*II*),  $\text{Ni}(\text{NCS})_2(4\text{-BrPy})_4$  (*III*),  $\text{Ni}(\text{NCS})_2(4\text{-CNPy})_4$  (*IV*) and  $\text{Ni}(\text{NCS})_2(4\text{-NH}_2\text{Py})_4$  (*V*). In complexes *I* and *II*, the loss of the volatile ligands R-Py (on the TG curve up to 573 K) occurs in two steps (-2, -2), and in complex *IV* in three steps (-2; -1.4; -0.6). Decomposition of complexes *III* and *V* is accompanied by ligand decomposition. The spectral data and magnetic moment values for all the initial complexes, together with the defined intermediates with composition  $\text{Ni}(\text{NCS})_2(4\text{-RPy})_2$ , indicated pseudooctahedral configuration.

The stoichiometry (step-wise character) of the thermal decomposition of compounds with the composition  $\text{NiX}_2\text{L}_4$  (X = anionic ligand, L = volatile nitrogen-containing ligand) may be either single-step or multi-step<sup>1</sup>. In single-step stoichiometry of the thermal decomposition, the ligands are lost simultaneously, which can be expressed by the equation



The decomposition occurs more frequently, however, in several steps, with step-wise loss of the volatile ligands. Depending on the crystal structure of the studied complexes and the experimental conditions, some of the steps are not observed. With complex compounds, it is necessary to also consider the properties of the central atom and of the ligands and their interactions. In the ligands, primarily the position and type of substituents are important, as they may affect the bonding properties of the donor atom as well as the stereochemistry of the initial complexes and their decomposition products<sup>1</sup>.

\* Part XVI in the series Heterogeneous reactions of solid nickel(II) complexes; Part XV: Chem. Zvesti, in press.

In work<sup>2</sup> we studied the effect of the positions of dialkyl-substituents on the pyridine molecule on the thermal properties of compounds with the composition  $\text{Ni}(\text{NCS})_2\text{L}_n$  ( $\text{L}$  = pyridine derivative). In this work the type of substituent is changed ( $\text{R}$  = Et, Cl, Br, CN and  $\text{NH}_2$ ) at constant position 4 on the pyridine ring.

## EXPERIMENTAL

### Preparation of the Initial Compounds

The synthesis was carried out using the chemicals 4-cyanopyridine, 4-aminopyridine, 4-ethylpyridine, 4-chloropyridine. HCl and 4-bromopyridine. HCl (Fluka AG, *purum*). Ethanol solutions of  $\text{Ni}(\text{NCS})_2$  were prepared by reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and KNCS (both *p.a.*, Lachema) dissolved in a suitable amount of ethanol, followed by filtration of the KCl precipitate formed.

$\text{Ni}(\text{NCS})_2(4\text{-EtPy})_4$  (*I*): To a solution of  $\text{Ni}(\text{NCS})_2$  (0.02 mol in 160 ml ethanol) was added with stirring 0.16 mol 4-EtPy. The finely crystalline purple product which formed immediately was left in the solution for 1 day and was then isolated, washed with diethyl ether and dried in the air. The compounds  $\text{Ni}(\text{NCS})_2(4\text{-CNPy})_4$  (*IV*) and  $\text{Ni}(\text{NCS})_2(4\text{-NH}_2\text{Py})_4$  (*V*) were prepared analogously.

$\text{Ni}(\text{NCS})_2(4\text{-ClPy})_4$  (*II*): A solution of 0.015 mol  $\text{Ni}(\text{NCS})_2$  was intensely stirred with 0.09 mol 4-ClPy (4-ClPy was prepared from 0.1 mol 4-ClPy.HCl and 0.15 mol NaOH in 40 ml  $\text{H}_2\text{O}$ ). The precipitate was separated, washed with a small amount of ethanol and dried in the air. Compound  $\text{Ni}(\text{NCS})_2(4\text{-BrPy})_4$  (*III*) was prepared analogously.

Defined decomposition products:  $\text{Ni}(\text{NCS})_2(4\text{-EtPy})_2$  (*VI*),  $\text{Ni}(\text{NCS})_2(4\text{-ClPy})_2$  (*VII*),  $\text{Ni}(\text{NCS})_2(4\text{-CNPy})_2$  (*VIII*) and  $\text{Ni}(\text{NCS})_2(4\text{-NH}_2\text{Py})_2$  (*IX*) were prepared by isothermal decomposition of the initial compounds  $\text{Ni}(\text{NCS})_2\text{L}_4$  at temperatures of 393, 348, 403 and 453 K. The results of the analyses are given in Table I. An intermediate, corresponding to the composition  $\text{Ni}(\text{NCS})_2(4\text{-CNPy})_{0.6}$  could not be prepared in a sufficient amount by isothermal decomposition in a pure form and consequently its existence as a separate chemical substance was not confirmed by further methods.

TABLE I  
Analysis of compounds *I–IX*

Compound	% Ni		% C		% H		% N	
	calc.	found	calc.	found	calc.	found	calc.	found
<i>I</i>	9.73	9.77	59.71	59.54	6.01	5.93	13.93	13.78
<i>II</i>	9.33	9.26	42.01	41.93	2.56	2.53	13.36	13.24
<i>III</i>	7.28	7.36	32.75	33.05	2.00	2.17	10.42	10.50
<i>IV</i>	9.91	10.03	52.73	53.10	2.72	2.86	23.65	23.62
<i>V</i>	10.65	10.68	47.93	47.63	4.39	4.51	25.40	25.58
<i>VI</i>	15.09	15.13	49.38	49.55	4.66	4.60	14.40	14.35
<i>VII</i>	14.61	14.46	35.86	36.05	2.01	2.20	13.94	13.82
<i>VIII</i>	15.29	15.38	43.79	43.84	2.10	2.24	21.89	21.65
<i>IX</i>	16.17	16.29	39.69	39.72	3.33	3.44	23.14	22.88

## Analytical Methods and Instruments

The contents of carbon, hydrogen and nitrogen were found using the Carlo Erba model 11-02 automatic elemental analyzer. The nickel content was determined complexometrically using murexide indicator.

The electronic spectra of the solid samples in nujol mulls were measured on a Unicam SP 700 C photophotometer. The magnetic susceptibility of the samples was measured at 293 K on a laboratory-constructed apparatus by the Gouy method. The thermal properties of the compounds were studied on a Derivatograph OD-102 instrument (MOM, Budapest). In all the thermal decompositions a sample weight of 100 mg was used and the rate of temperature increase was  $3 \text{ K} \cdot \text{min}^{-1}$ . The measurement was carried out in the air using a crucible consisting of four platinum dishes (platinum polyplate).

## RESULTS AND DISCUSSION

*The Thermal Properties of the Studied Complex Compounds*

The following conclusions can be drawn from the data obtained from the TG, DTA and DTG curves for complexes I-V, given in Table II: Complex I is thermally stable up to 343 K, complex II to 323 K, Complex III to 343 K, complex IV to 378 K and complex V to 423 K (according to the beginning of mass loss). Thus, the initiation of mass loss on the TG curves indicates that the thermal stability of the

TABLE II  
Data from the TG, DTG and DTA curves for complexes of the type  $\text{NiL}_4(\text{NCS})_2$  [L = 4-RPy]

Complex	$T_{\text{decomp.}}$ , K	TG, %		DTA, K		DTG, K	
		-2 L calc./found	-4 L calc./found	$T'_{\text{max}}^a$	$T''_{\text{max}}$	$T'_{\text{max}}$	$T''_{\text{max}}$
I	343	35.5 36.0	71.0 71.0	423	473	413	468
II	323	36.1 35.5	72.2 72.0	373	458	373	458
III	343	—	—		393 (exo)		388
IV	378	35.3 35.0	70.4 71.0	413	478 ~530	413	473 528
V	423	34.1 34.5	—	488	543 (exo)	488	533

<sup>a</sup>  $T_{\text{max}}$  corresponds to the temperature of maximal deviations on the DTA or DTG curve.

studied complexes increases according to the type of substituent R in the order:  $\text{Cl} < \text{Br} \approx \text{Et} < \text{CN} < \text{NH}_2$ .

The TG and DTG curves indicate that the loss of the volatile nitrogen-containing ligands (endothermic processes on the DTA curves) for complexes *I* and *II* occurs in two steps (Fig. 1) and in three steps for complex *IV*. With complex *IV*, however, the ligands are lost in non-integral numbers. With complex *III* (Fig. 2) the ligands decompose in the given temperature interval, reflected in a marked exothermic effect on the DTA curve. With complex *V*, the ligands decompose only after loss of two 4- $\text{NH}_2\text{Py}$  molecules. The loss of the volatile nitrogen-containing ligands can be expressed briefly in terms of the following schemes:

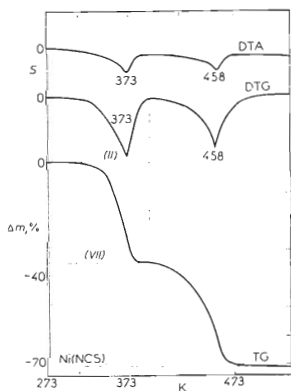
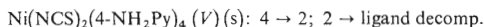
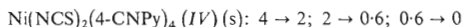
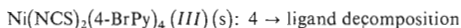
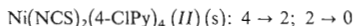
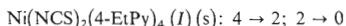


FIG. 1

The TG, DTG and DTA curves of the complex  $\text{Ni}(\text{NCS})_2(4\text{-ClPy})_4$  (*II*)

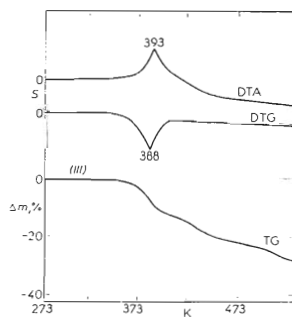


FIG. 2

The TG, DTG and DTA curves of the complex  $\text{Ni}(\text{NCS})_2(4\text{-BrPy})_4$  (*III*)

*The Magnetic and Spectral Properties of the Studied Complexes and Their Stereochemistry*

The values of the magnetic moments  $\mu_{\text{eff}}$  (B.M.) and the positions of the maxima of the absorption bands in the electronic spectra of the studied complexes with composition  $\text{Ni}(\text{NCS})_2(4\text{-RPy})_n$  ( $n = 4$  or  $2$ ) are given in Table III.

On the basis of the electronic absorption spectra (depending on the number and positions of the bands) the studied compounds can be divided into two groups. The first group includes compounds *I* to *V*, *i.e.* with composition  $\text{Ni}(\text{NCS})_2(4\text{-RPy})_4$ ; the second contains compounds *VI* to *IX*, *i.e.* with the composition  $\text{Ni}(\text{NCS})_2 \cdot (4\text{-RPy})_2$ .

All the complexes in the first group have an effective magnetic moment in the interval given for hexacoordinated octahedral complexes<sup>2,3</sup>. The electronic spectra of these complexes in the region 8 000 to 30 000  $\text{cm}^{-1}$  contain three broad but simple bands with relatively low intensity. The positions of the maxima of the absorption bands in the region 26 000–28 000  $\text{cm}^{-1}$  cannot be found precisely because of their partial overlap with the charge transfer bands. The number of bands, their width and the positions of the absorption maxima on these bands indicate pseudooctahedral configuration<sup>4</sup> of the ligands around the Ni(II) atom.

TABLE III

The magnetic moments and wavenumbers of the maxima of the bands in the electronic absorption spectra of the  $\text{Ni}(\text{NCS})_2(4\text{-RPy})_n$  complexes ( $n = 4$  or  $2$ )

Compound	$\mu_{\text{eff}}$ B.M.	$\tilde{\nu}_{\text{max}}$ , $\text{cm}^{-1}$		
<i>I</i>	3·14	10 700	17 250	26 000–28 000
<i>II</i>	3·13	10 300	16 700	26 000–28 000
<i>III</i>	3·14	10 650	17 200	26 000–28 000
<i>IV</i>	3·20	10 700	17 300	26 000–28 000
<i>V</i>	3·20	10 700	17 600	27 000–28 000
<i>VI</i>	3·18	8 200	16 450	—
		11 100 (sh) <sup>a</sup>		
<i>VII</i>	3·16	9 700	16 100	—
<i>VIII</i>	3·28	9 000		
		11 200 (sh)	16 400	—
<i>IX</i>	3·24	8 400	16 500	—
		11 200 (sh)		

<sup>a</sup> sh = shoulder.

Similarly, the complexes in the second group have  $\mu_{\text{eff}}$  values in a region typical for octahedral nickel complexes. The first bands located in the region 8 000 to 11 5000  $\text{cm}^{-1}$  exhibit pronounced splitting; on the higher energy side are located shoulders or even separate bands. The positions of these bands cannot be found in the region 26 000 to 28 000  $\text{cm}^{-1}$  because of marked overlap with the charge transfer bands. The positions of these bands are markedly shifted to lower energy values compared to those for the complexes in the first group. The spectral data also indicate pseudo-octahedral configuration<sup>4</sup> for the studied complexes.

In conclusion, it appears that pseudo-octahedral configuration is most probable for all the initial complexes as well as for their decomposition products  $\text{Ni}(\text{NCS})_2 \cdot (4\text{-RPy})_2$ , in spite of the different inductive effects of the various substituents. Apparently position 4, which is rather far from the donor atom, weakens this electron effect (and prevents steric effects), which is marked in position 2. Complexes with composition  $\text{Ni}(\text{NCS})_2(2\text{-RPy})_2$  with  $\text{R} = \text{Me}$  or  $\text{Et}$  are square (+I-effect of the substituents ensures the stability of these complexes), while complexes with  $\text{R} = \text{Cl}$ ,  $\text{Br}$  and  $\text{CN}$  are polymerically octahedral (-I-effect of the substituents decreases the electron density on the heterocyclic nitrogen atoms and limits the possibility of formation of stable tetracoordinated square-planar complexes)<sup>5</sup>.

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Translated by M. Štulíková.