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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES XXIV

Stoichiometry of thermal decomposition and stereochemistry of thiocyanate nickel(II) complexes with piperidine ligands

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The stoichiometry of thermal decomposition was studied for the following compounds: $Ni(NCS)_2(pip)_4$ (I), (*pip* = piperidine), $Ni(NCS)_2(pip)_4py \cdot H_2O$ (II), (*py* = piridine), $Ni(NCS)_2(4\text{-}Mepip)_3$ (III), $Ni(NCS)_2(3\text{-}Mepip)_3$ (IV) and $Ni(NCS)_2(3.5\text{-}Me_2pip)_3$ (V). In complexes I, II, III and IV the loss of the volatile ligands (on the TG curve to 300 °C) occurs in three steps and in complex V in two steps. The loss of the last molecules of volatile ligands is accompanied by the decomposition of NCS groups. Spectral data and magnetic moment values for the initial complexes I and II (together with the defined intermediates) indicated pseudooctahedral configuration while pentacoordination for complexes III, IV and V. Structural changes of the complexes studied in thermal decomposition reactions are discussed.

Recently it was shown [1–5] that the stoichiometry of the thermal decomposition reactions and stereochemical changes of thiocyanate nickel(II) complexes with pyridine derivatives in thermal decomposition depend on the properties of the heterocyclic ligands. In this paper the attention was focussed to thiocyanate nickel(II) complexes with piperidine ligands which are saturated analogues of pyridine derivatives. It was expected that a change of the position of methyl substituents in the piperidine ring could also influence stereochemical changes in the thermal decomposition reactions of the complexes studied. On the other hand, same derivatives of piperidine and also various nickel(II) complexes [6, 7] quench the reactions of singlet oxygen (use as plastic additives). From this aspect decided to study of thermal, spectral and magnetic properties of the thiocyanate nickel(II) complexes with piperidine ligands.

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Experimental

Preparation of starting compounds

The starting complexes were prepared by the following general method: a suspension of 0.01 mol of $Ni(NCS)_2$ was made with 50 cm^3 benzene, then 0.1–0.2 mol of piperidine ligand was added. This system had been boiled and stirred under reflux for cca. 5 h. Then the solution was poured into a crystallizing dish and let crystallise freely for 15–20 h. The products with composition $Ni(NCS)_2(pip)_4$ (I) and $Ni(NCS)_2L_3$ (L = 4-Mepip, 3-Mepip and 3.5-Mepip) (III, IV and V) were washed with ethanol and ether and dried in a desiccator over P_2O_5. Complex II was prepared by recrystallization of complex I from 10% solution of piperidine in benzene. The X-ray structure analysis confirmed the formula $Ni(NCS)_2(pip)_4py \cdot H_2O$ [8]. The pyridine was probably present as an impurity in the piperidine used for recrystallization.

Table 1 Analytical data for complexes with piperidine ligands

Complex		Ni, %		C, %		H, %		N, %	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
$Ni(NCS)_2(pip)_4$	(I)	11.39	11.55	51.26	50.68	8.54	8.37	16.30	15.92
$Ni(NCS)_2(pip)_4py \cdot H_2O$	(II)	9.58	9.70	52.94	52.10	8.26	8.32	16.01	15.67
$Ni(NCS)_2(4\text{-}Mepip)_3$	(III)	12.45	12.43	50.82	50.78	8.25	7.99	14.83	14.70
$Ni(NCS)_2(3\text{-}Mepip)_3$	(IV)	12.45	12.40	50.82	50.70	8.25	8.10	14.83	14.72
$Ni(NCS)_2(3.5\text{-}Me_2pip)_3$	(V)	11.41	11.57	53.66	53.84	8.76	8.57	13.60	13.66
$Ni(NCS)_2(pip)_2$	(VI)	17.10	16.89	41.72	41.93	6.37	6.35	16.24	16.42
$Ni(NCS)_2(4\text{-}Mepip)_2$	(VII)	15.74	16.06	45.07	44.62	7.02	7.05	15.02	15.28
$Ni(NCS)_2(3\text{-}Mepip)_2$	(VIII)	15.74	15.88	45.07	44.70	7.02	6.98	15.02	15.17
$Ni(NCS)_2(3.5\text{-}Me_2pip)_2$	(IX)	14.63	14.70	47.89	47.00	7.48	7.41	13.96	13.78
$Ni(NCS)_2(pip)_1$	(X)	22.58	22.49	32.33	31.88	4.26	4.28	16.16	16.32
$Ni(NCS)_2(4\text{-}Mepip)_1$	(XI)	21.42	21.30	35.06	36.12	4.78	4.88	15:34	15.42
$Ni(NCS)_2(3\text{-}Mepip)_1$	(XII)	21.42	21.33	35.06	35.80	4.78	4.92	15.34	15.48

$Ni(NCS)_2(pip)_2$ (VI), $Ni(NCS)_2(4\text{-}Mepip)_2$ (VII), $Ni(NCS)_2(3\text{-}Mepip)_2$ (VIII), $Ni(NCS)_2(3.5\text{-}Me_2pip)_2$ (IX), $Ni(NCS)_2(pip)_1$ (X), $Ni(NCS)_2(4\text{-}Mepip)_1$ (XI) and $Ni(NCS)_2(3\text{-}Mepip)_1$ (XII) complexes were prepared by the izothermal decomposition of starting complexes at 90° (complex VI, VII, VIII and IX) and 180° (complex X, XI and XII). The analytical data are given in Table 1.

Analytical methods and equipment

The analytical methods were described in papers [1–5]. The thermal properties of the compounds were studied on a Derivatograph OD 102 instrument. In all thermal decompositions a sample weight of 100 mg was used and the rate of temperature increase was 3 deg/min. The measurements were carried out in air using a platinum crucible. the electronic spectra of the solid samples were measured on a Unicam SP 700 photometer. Infrared absorption spectra were recorded with a UR model 20 spectrophotometer. Magnetic moments were measured with a Goy balance at room temperature.

Results and discussion

Thermal properties of the complexes studied

The data obtained from the TG, DTG and DTA curves for complexes I–V (Table 2) permit the following conclusions: complex I is thermally (for the kinetics see [9]) stable up to 50°, complex II to 45°, complex III to 65°, complex IV to 70° and complex V to 70° (considering the beginning of mass loss). Thus, the initiation of mass loss on the TG curve indicates that the thermal stability of studied complexes increases in the order

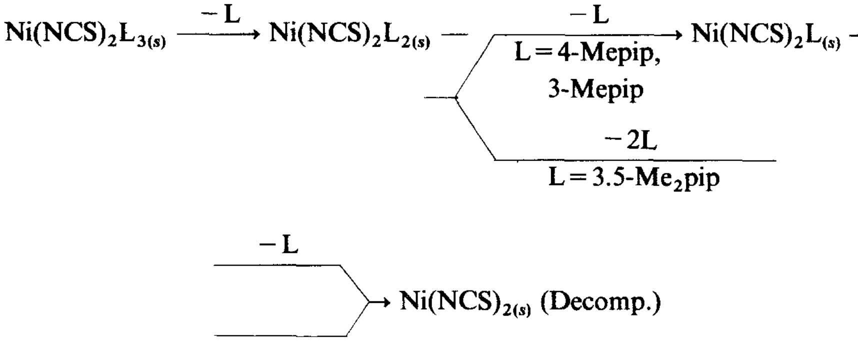
$$\mathrm{Ni(NCS)_2L_4} < \mathrm{Ni(NCS)_2L_3}.$$

The TG and DTG curves indicate that the loss of the volatile ligands for $\mathrm{Ni(NCS)_2L_4}$ complexes (I and II) occurs in three steps (Table 2):

$$\begin{tikzcd} \mathrm{Ni(NCS)_2(pip)_{4(s)}\ (I)} \arrow[dr, "-2\ \mathrm{pip}"] & & \\ & \mathrm{Ni(NCS)_2(pip)_2} \arrow[r, "-\mathrm{pip}", "(s)"'] & {} \\ \mathrm{Ni(NCS)_2(pip)_4\cdot py\cdot H_2O_{(s)}\ (II)} \arrow[ur, "-2\ \mathrm{pip}", "-\mathrm{py},\ -\mathrm{H_2O}"'] & & \end{tikzcd}$$

$$\rightarrow \mathrm{Ni(NCS)_2(pip)_{1(s)}} \xrightarrow{-\mathrm{pip}} \mathrm{Ni(NCS)_{2(s)}}\ \text{(Decomp.)} \qquad (1)$$

With complexes of the type $\mathrm{Ni(NCS)_2L_3}$ the volatile ligands have been found to leave either in three steps (complex III and IV) or in two steps (complex V) according to the scheme:



$$\mathrm{Ni(NCS)_2L_{3(s)}} \xrightarrow{-L} \mathrm{Ni(NCS)_2L_{2(s)}} \begin{cases} \xrightarrow[\mathrm{L = 4\text{-}Mepip,\ 3\text{-}Mepip}]{-L} \mathrm{Ni(NCS)_2L_{(s)}} \xrightarrow{-L} \\ \xrightarrow[\mathrm{L = 3.5\text{-}Me_2pip}]{-2L} \end{cases} \mathrm{Ni(NCS)_{2(s)}}\ (\text{Decomp.}) \qquad (2)$$

The release of volatile ligands takes places in well-defined steps, which can be clearly observed on the TG and DTG curves (Figs 1 and 2). The loss of the last molecules of piperidine is accompanied by decomposition of NCS groups as shown by an expressive exothermic peak on the DTA curves (Figs 1 and 2, Table 2).

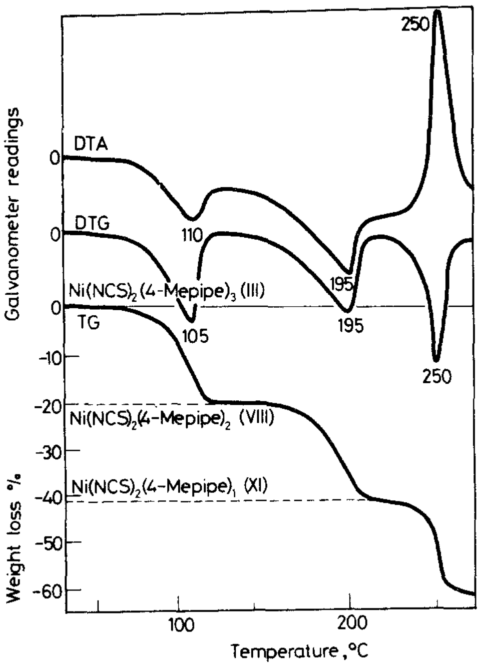


Fig. 1 Thermal curves of $Ni(NCS)_2(4\text{-}Mepip)_3$ (III)

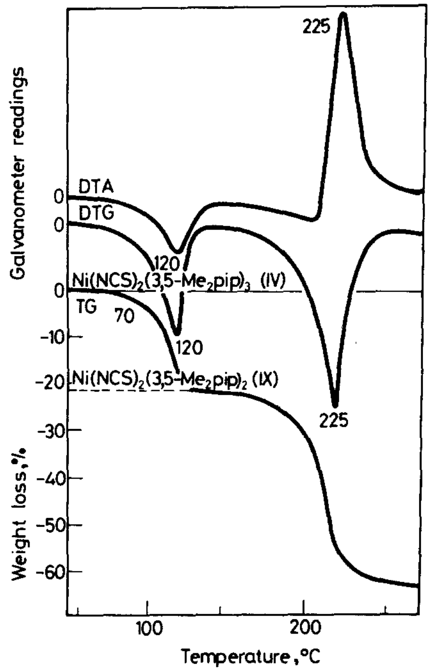


Fig. 2 Thermal curves of $Ni(NCS)_2(3.5\text{-}Me_2pip)_3$ (IV)

Table 2 Data of the TG, DTG and DTA curves

Complex		$T_{decomp.}$[a]	TG, % calcd. /found			DTG, °C			DTA, °C		
$Ni(NCS)_2(pip)_4$	(I)	50	33.4 32.5	16.5 16.0	16.5 16.0	100	200	245	100	200	245[b]
$Ni(NCS)_2(pip)_4py \cdot H_2O$	(II)	45	43.7 43.0	13.9 14.0	13.9 15.0	80 95	200	250	80 95	200	250[b]
$Ni(NCS)_2(4\text{-}Mepip)_3$	(III)	65	21.0 20.5	21.0 21.5	21.0 24.0	105	195	250	110	195	250[b]
$Ni(NCS)_2(3\text{-}Mepip)_3$	(IV)	70	21.0 20.0	21.0 20.0	21.0 20.0	100	210	250	100	210	260[b]
$Ni(NCS)_2(3.5\text{-}Me_2pip)_3$	(V)	70	22.0 22.0	44.0 43.0		175	280		150 190	280[b]	

[a] according to the beginning of mass loss (°C)

[b] the exothermic peak (the complexes are completely decomposed)

The spectral and magnetic properties of initial complexes and defined intermediates

The complexes I and II have an effective magnetic moment and maxima of absorption bands in the interval given for hexacoordinated pseudooctahedral complexes (Table 3) [10, 15, 16]. A strong absorption band ν(C—N) at 2090 cm^{-1} (complex I) and 2080 cm^{-1} (complex II) indicate monomeric structure with unidentate NCS groups [11, 15]. This is in agreement with the results of the X-ray structure analysis [8, 12]. The equatorial plane of the $Ni(NCS)_2(pip_4$ (I) is formed by four N atoms from the piperidine molecules and the axial positions are occupied by two N atoms from the NCS groups. Structural data [8] show further that for complex II the Ni(II) atom is pseudooctahedrally coordinated by two N atoms from the NCS groups, two N atoms from the piperidine molecules, one N atom from the pyridine molecule and one O atom from the coordinated water molecule. The next two piperidine molecules are bonded by hydrogen bonds with the water molecule. Thus, the composition of complex II should be written as $(Ni(NCS)_2(pip)_2pyH_2O]\cdot 2pip$.

The effective magnetic moment, the number and position of the bands of electronic absorption spectra seem to support the assumption of pentacoordinated $Ni(NCS)_2L_3$ complexes (Table 3) [2, 13]. In similar complex $Ni(NCS)_2(2.6\text{-}Me_2py)_3$ the trigonal-bipyramidal configuration was confirmed by X-ray structure analysis [14]. Pentacoordination of complex III, IV and V requires terminally-bonded NCS groups (ν(C—N) at about 2080 cm^{-1}). The splitting of ν(C—N) bands can be connected to the nonlinearity of NCS groups or interactions in crystal structure [11].

On the basis of magnetic and spectral data (Table 3) $Ni(NCS)_2L_2$ complexes show pseudooctahedral configuration. A strong absorption band at about 2120 cm^{-1} in infrared spectra indicate polymeric structure with bidentate NCS groups [11, 15], in analog with the similar complex $Ni(NCS)_2py_2$ [17]. The first band in the electronic absorption spectra in the region 8,000 to 12,000 cm^{-1} exhibit pronounced splitting. With respect to the predicted NiN_4S_2 chromophore a marked tetragonal distortion is likely in these complexes.

The $Ni(NCS)_2L$ complexes (X, XI and XII) have a polymeric pseudooctahedral configuration. With the decrease in the number of heterocyclic ligands coordinated to Ni(II), the hexacoordination of these complexes is completed by the adjacent structure units.

Thermal structural transformations

Structural changes during the thermal decomposition reactions are summarized in Table 4. On the basis of the data in Table 4 the following conclusions can be derived:

Table 3 Values of magnetic moments and positions of absorption bands in electronic (d–d) spectra and IR spectra for complexes with piperidine ligands

Complex		μ_{eff}, B.M.	Maxima of absorption bands					
			Electronic spectra, cm^{-1}				IR spectra, cm^{-1}	
							ν(CN)	ν(CS)
$Ni(NCS)_2(pip)_4$	(I)	3.29		9000	15000, 26000		2090	800
$Ni(NCS)_2(pip)_4py \cdot H_2O$	(II)	3.12		9600	15800, 25700		2080	810
$Ni(NCS)_2(4\text{-}Mepip)_3$	(III)	3.23	6200,	11500(br)[a],	15400, 21500(sh)[b],	24750	2080 2070	810
$Ni(NCS)_2(3\text{-}Mepip)_3$	(IV)	3.20	6100,	11600(br),	15500, 21700(sh),	24800	2090 2078	800
$Ni(NCS)_2(3.5\text{-}Me_2pip)_3$	(V)	3.20	600,	11700(br),	15400, 21500(sh),	25000	2080 2065	798
$Ni(NCS)_2(pip)_2$	(VI)	3.18	8200,	10600	16100, 29900		2120	800
$Ni(NCS)_2(4\text{-}Mepip)_2$	(VII)	3.17	8100,	10600	16000, 29600		2120	810
$Ni(NCS)_2(3\text{-}Mepip)_2$	(VIII)	3.19	8000,	10500	16000, 29900		2120	800
$Ni(NCS)_2(3.5\text{-}Me_2pip)_2$	(IX)	3.17	8200,	10600	16200, 29800		2120	790
$Ni(NCS)_2(4\text{-}Mepip)_3$	(X)	paramm.[c]	7600(sh),	9000	15400, 26000		2120 2150(sh)	810 780
$Ni(NCS)_2(4\text{-}Mepip)_1$	(XI)	paramm.[c]	7800(sh),	9200	15500, 26000		2120 2150(sh)	810 780
$Ni(NCS)_2(3\text{-}Mepip)_1$	(XII)	paramm.[c]	7800(sh),	9100	15500, 26100		2122 2140(sh)	800 780

[a] br – broad, [b] sh – shoulder, [c] the amount of sample was not sufficient for a precise measurement of μ_{eff}

i) For all initial complexes and intermediates with piperidine (with no substituent on the piperidine ring) only the pseudooctahedral configuration was found to exist and the transformation

$$\begin{gathered}\text{monomeric pseudooctahedral-Ni(NCS)}_2\text{L}_4 \rightarrow \text{polymeric} \\ \text{pseudooctahedral-Ni(NCS)}_2\text{L}_2 \text{ (or Ni(NCS)}_2\text{L)}\end{gathered} \tag{3}$$

takes place during the thermal decomposition of this complexes.

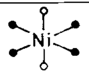
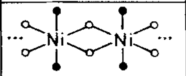
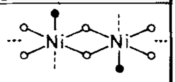
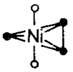
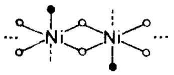
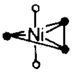
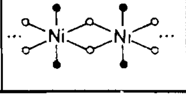
ii) the initial complexes with methyl substituent in the 4- or 3-position on the piperidine ring are pentacoordinated and the stereochemical change

$$\begin{gathered}\text{trigonal bipyramidal-Ni(NCS)}_2\text{L}_3 \rightarrow \text{polymeric pseudoocta-} \\ \text{hedral-Ni(NCS)}_2\text{L}_2 \text{ (or Ni(NCS)}_2\text{L)}\end{gathered} \tag{4}$$

proceeds during the thermal decomposition reactions.

Table 4 Thermal structural changes in $Ni(NCS)_2L_n$ complexes[a]

[a] – ● piperidine derivatives; ○ NCS group

L	n			
	4	3	2	1
pip				
4-Mepip 3-Mepip	–			
3,5-Me$_2$ pip	–			a) ●-piperidine derivatives o-NCS groups

Thus, primarily the properties of the ligands (the presence of the methylsubstituent on the piperidine ring) affect the bonding ability of the donor atom as well as the stereochemistry of the initial complexes and their decomposition products [1–5].

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Zusammenfassung — Die Stöchiometrie der thermischen Zersetzung folgender Verbindungen wurde untersucht: $Ni(NCS)_2(pip)_4$ (I), (*pip* = Piperidin), $Ni(NCS)_2(pip_4)py \cdot H_2O$ (II) (*py* = Pyridin), $Ni(NCS)_2(4\text{-}Mepip)_3$ (III), $Ni(NCS)_2(3\text{-}Mepip)_3$ (IV) und $Ni(NCS)_2(3{,}5\text{-}Me_2pip)_3$ (V). Bei den Komplexen I, II, III und IV vollzieht sich die Abgabe der flüchtigen Liganden (lt. TG-Kurve bis 300 °C) in drei, beim Komplex V in zwei Schritten. Der Verlust des letzten flüchtigen Ligandenmoleküls wird durch die Zersetzung der NCS-Gruppe begleitet. Auf Grund der Spektrenangaben und der Dipolmomentwerte der Ausgangskomplexe I und II (zusammen mit den bekannten Intermediären) kann auf eine pseudooktaedrische Konfiguration, bei den Komplexen III, IV und V auf eine Pentakoordination geschlossen werden. Strukturveränderungen der untersuchten Komplexe während der thermischen Zersetzungsreaktionen werden besprochen.

Резюме — Изучена стехиометрия термического разложения комплексов $Ni(NCS)_2(pip)_4$ (I), $Ni(CS)_2(pip_4)py \cdot H_2O$ (II), $Ni(NCS)_2(4\text{-}Mepip)_3$ (III), $Ni(NCS)_2(3\text{-}Mepip)_3$ (IV) и $Ni(NCS)_2(3{,}5\text{-}Me_2pip)_3$ (V); где *py* = пиридин и *pip* = пиперидин. В комплексах I–IV выделение лигандов (на кривой ТГ до 300°) происходит в три стадии, тогда как для комплекса V — в две стадии. Потеря последних молекул органических лигандов сопровождается разложением тиоцианатных групп. Спектральные данные и величины магнитных моментов для исходных комплексов I и II, совместно с их промежуточными продуктами разложения, указывают на их псевдооктаэдрическую конфигурацию, а для комплексов III–V — пятикоординационную. Обсуждены структурные изменения комплексов в процессе реакций их термического разложения.